Theoretical Design of Hexacoordinate Hypervalent Carbon Compounds by Analyzing Substituent Effects

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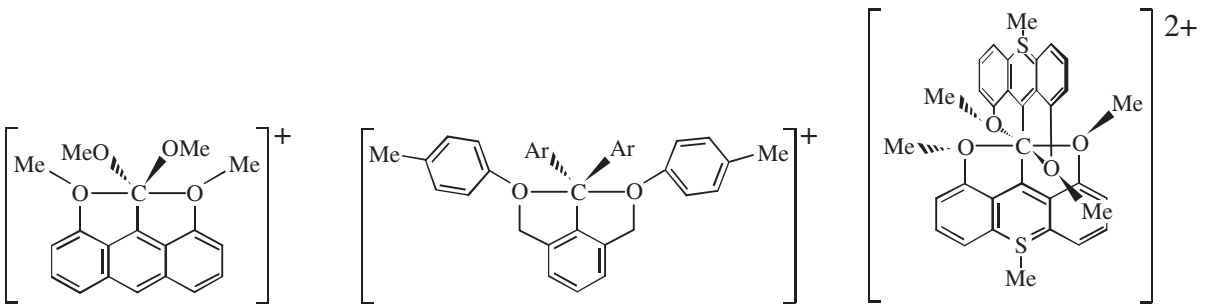
A hexacoordinate hypervalent carbon compound with an ideal octahedral structure was proposed theoretically in a previous study (*Chem. Phys. Lett.* **2008**, *460*, 37). However, there is no report telling of success in synthesizing the compound and/or its derivatives. In order to perform a theoretical design for stronger hypervalent bonds, the present study systematically investigated the substituent effects at the para position of phenyl groups of axial C–C and equatorial C–O bonds by adopting 14 functional groups involving both electron-donating and -withdrawing groups. The results showed that the substituent effect at the former position is more influential than that at the latter. In the former case, a good correlation between the C–C and C–O distances is found and the hypervalent C–O bonds are strengthened as the substituent becomes more electron-withdrawing. In the latter case, both electron-donating and -withdrawing groups slightly weaken the hypervalent C–O bonds.

The concept of hypervalent compounds was established by Musher in 1969.[1] The definition of hypervalent compound was extended as a main group element compound which contains a number of formally assignable electrons of more than the octet in a valence shell directly associated with the central atom.[2,3] Molecular orbital (MO) theory could explain the extra electrons possessed by the central atom in terms of three-center four-electron (3c-4e) bonds as early as 1951.[4,5]

While various hypervalent compounds of heavy main group elements have been prepared, those of carbon, which is the central element of organic chemistry, have been remarkably scarce. Akiba and co-workers synthesized pentacoordinate hypervalent carbon compounds, **1** and **2** (Chart 1).[6–8] Furthermore, a hexacoordinate hypervalent carbon compound **3** was reported by the same group.[9] X-ray diffraction reveals that the structure of **3** is considerably bent at the 3c-4e bond.

In our theoretical research,[10] alternative hexacoordinate hypervalent carbon compounds **4** and **5** were discovered (Chart 2). Their structures are more ideal than **3**: namely, the O–C–O bond angles are quasi-linear. The C–O bond distances, in particular, in **5** are shorter than those in **4**. While the group of Akiba and Yamamoto has been trying to synthesize **5** and its derivatives, bearing electron-donating group such as NMe_2 and OPh as para substituent (X) in **6**, they have not succeeded in synthesizing them so far. To the best of our knowledge, there is no report of the synthesis of hexacoordinate hypervalent carbon compounds other than **3**.

The present study attempts to clarify the electronic effect to strengthen (or weaken) the 3c-4e bonds by substituting functional groups in compound **5** in order to perform theoretical design of hexacoordinate hypervalent carbon compounds. The organization of this paper is as follows. Computational details are described in the second section. The third section shows results and discussion. Finally, concluding remarks are given.



1 **2** **3**

Chart 1.

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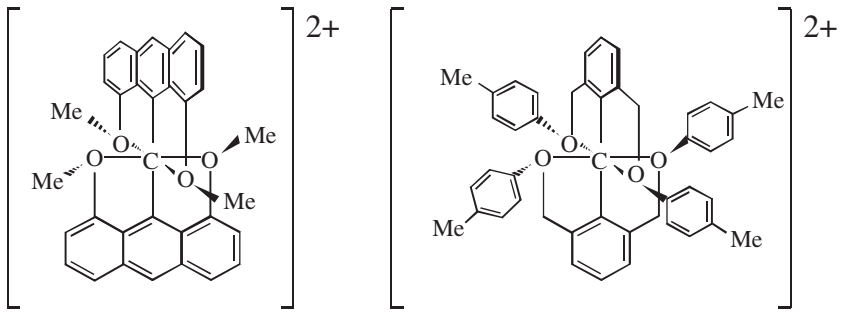
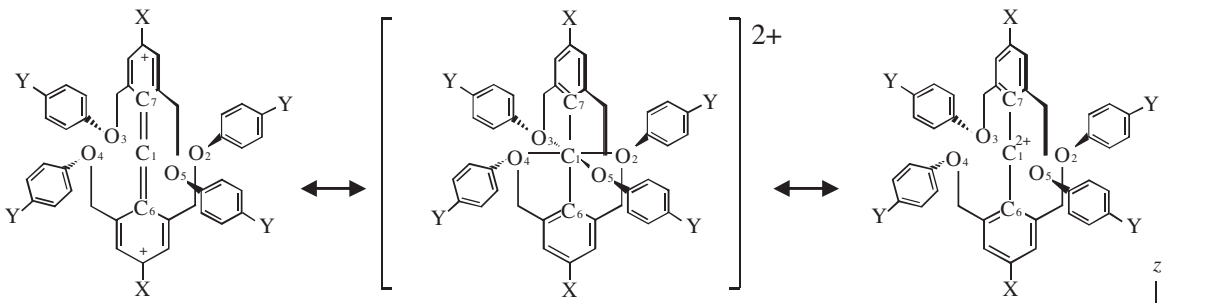


4 **5**

Chart 2.



6a **6b** **6c**

Figure 1. Three resonance structures of compound **6** in which positions X and Y are substituted by 14 functional groups. The axial C–C bonds are situated along the z axis and the equatorial C–O bonds along x and y axes.

Computational Details

The present study examined the substituent effect at X and Y positions in compound **6** shown in Figure 1. Both X and Y are situated at the para position of phenyl groups of the axial C–C and equatorial C–O bonds regarding the central carbon atom, respectively. Since ortho or meta substitution involves not only electronic effects but also steric effects, we examine only para substitution in order to investigate the electronic effects of substitution on the 3c-4e bond. Furthermore, such steric repulsion appears to hinder the synthesis of the compound. 14 Functional groups, i.e., NMe_2, NH_2, OH, OMe, Me, H, F, Cl, COOH, COOMe, COMe, CF_3, CN, and NO_2, were employed as substituents. These involve both electron-donating and -withdrawing groups as represented by the indices of Hammett's σ_p in Table 1, which are determined by reaction rates and equilibrium constants of para-substituted benzoic acid derivatives.[11,12] As shown in Table 1, the derivatives are numbered **X1** to **X14** when X is substituted by the above 14 groups in keeping Y = Me. Similarly, the derivatives of **Y1** to **Y14** are defined for the substitutions of Y in maintaining X = H. Since **X6** is identical to **Y5** and further to the original compound **5**, a total of 27 compounds were examined in this study. In the end of the next section, we also discuss a compound with $X = NO_2$ and Y = H.

Geometry optimizations of the derivatives were carried out by density functional theory (DFT) calculations with the B3LYP hybrid functional[13] which consists of the Hartree–Fock exchange, the Slater exchange,[14] the Becke exchange,[15] the Vosko–Wilk–Nusair correlation,[16] and the Lee–Yang–Parr correlation[17] functionals. As for the Gaussian basis sets, the correlation-consistent valence double-zeta with polarization (cc-pVDZ) sets of Dunning[18,19] were employed for all atoms. In order to confirm that the obtained structures correspond to potential minima, frequency analyses were performed at the same level: namely, B3LYP/cc-pVDZ. The DFT calculations were performed by using the Gaussian09 suite of programs.[20]

Table 1. Substituents and Hammett's σ_p Values

Entry		Substituent	σ_p
X (Y = Me)	Y (X = H)		
X1	**Y1**	NMe_2	−0.83
X2	**Y2**	NH_2	−0.63
X3	**Y3**	OH	−0.37
X4	**Y4**	OMe	−0.27
X5	**Y5**	Me	−0.17
X6	**Y6**	H	0.00
X7	**Y7**	F	0.06
X8	**Y8**	Cl	0.23
X9	**Y9**	COOH	0.45
X10	**Y10**	COOMe	0.45
X11	**Y11**	COMe	0.50
X12	**Y12**	CF_3	0.54
X13	**Y13**	CN	0.66
X14	**Y14**	NO_2	0.78

The standard method to evaluate the bond energy, which reveals the energy difference between the binding and dissociating systems for a specific bond, cannot be applied to the systems in which the fragments interact with each other at multiple positions. On the other hand, the bond energy density analysis (Bond-EDA)[21] evaluates the bond energies in such multi-interacting systems, because it only requires the electronic-structure information of the combined system, not that of the separated system. The physical meaning of the bond energy is slightly different between the standard method and Bond-EDA. While the former includes geometric and/or electronic relaxations, the latter does not. Thus, Bond-EDA tends to give larger bond energies compared to the standard method. For example, the C–C bond dissociation energies calculated at the B3LYP/cc-pVDZ level are 94.3 and 177.7 kcal mol^{-1} for ethane and ethylene, respectively.[10] The corresponding experimental values are 90.2 and 174.5 kcal mol^{-1}.[22] On the other hand, the C–C bond energies estimated by Bond-EDA are 148.4 and 212.1 kcal mol^{-1} at the B3LYP/cc-pVDZ level.[10] The details of Bond-EDA are explained in Ref. 21 and several studies applied it to various chemical processes demonstrated its usefulness.[10,23,24] In Ref. 10, for example, Bond-EDA was employed to evaluate the 3c-4e bond of **5**. Moreover, in Ref. 23, Bond-EDA was applied to the analysis of the bond-alternation between single and the double bonds, accompanying a Diels–Alder reaction. In addition to those chemical bonds, Bond-EDA was successfully used to evaluate the weak interaction (ca. 33 kcal mol^{-1}) between the reactants in the transition state. Thus, the bond energies estimated by Bond-EDA are reliable for evaluating bond strength tendency in a dimension of energy. Since the central carbon atom in the present systems, **X1**–**X14** and **Y1**–**Y14**, interact at multiple positions, we adopted Bond-EDA to evaluate the bond energy. The Bond-EDA calculations were carried out by linking the original code with GAMESS program package.[25]

Results and Discussion

Geometry optimizations have been accomplished for 27 derivatives, i.e., **X1**–**X14** and **Y1**–**Y14** (**X6** = **Y5**), of which geometric parameters are summarized in the Supporting Information. The frequency analyses revealed that all the optimized structures except for **X5** are stable with no frequency modes with negative eigenvalues. The two normal modes with negative frequencies, i.e., 47.7i and 26.0i cm^{-1}, in **X5** correspond to the internal rotation of methyl groups, which shall not affect the stability of the compound significantly. The summary of the frequency analyses are also presented in the Supporting Information.

Let us first discuss the chemical bonds around the central carbon atom in **X1**–**X14** and **Y1**–**Y14**: namely, axial C–C and equatorial C–O bonds. The C–C distances in the 27 compounds are in the range of 1.338–1.376 Å. Since the lengths of typical C–C single, double, and triple bonds are 1.54, 1.34, and 1.20 Å, respectively,[22] the axial C–C bonds in the 27 compounds correspond to a double bond. Namely, the axial C_6–C_1–C_7 bond shows allenic interaction character, i.e., C=C=C. As is well-known, the sp hybridized orbitals of the central carbon atom form the σ bonds while the other 2p orbitals, i.e., $2p_x$ and $2p_y$ contribute to the π bonds. It is noted that the C–C distances in the 27 compounds are slightly longer than that of allene, namely, 1.31 Å.[22]

The C–O distances are in the range of 2.445–2.724 Å, which are considerably longer than the covalent C–O bond: namely, 1.42 Å.[22] However, it was mentioned in an experimental study[9] that analysis of the Cambridge crystal database reveals ca. 2000 structures of the type O···CR_2 with the distances in the range of 2.6–2.8 Å. Many could be classified as at least pentacoordinate.

Theoretical study[6–8] also proved the existence of the weakly bonding interactions for such distant bonds. The interaction was assigned to the 3c-4e bond since corresponding bonding, nonbonding, and antibonding MOs were obtained.[10] Similarly, MO analyses in the 27 compounds clarified the existence of the 3c-4e bond except for **X1**. For example, the bonding, nonbonding, and antibonding orbitals in **X14** are shown in Figure 2. The MOs for the 3c-4e bond in **X2**–**X13** and **Y1**–**Y14** are given in the Supporting Information. Namely, the $2p_x$ and $2p_y$ orbitals of the central carbon atom partially contribute to the 3c-4e bond in addition to the π bonds for the axial allenic interaction.

Let us next discuss the substituent effect at the X position. The variation of the bond distances appeared mainly in the equatorial C–O bonds regarding the central carbon atom: namely C_1–O_2, C_1–O_3, C_1–O_4, and C_1–O_5. Maximum variation of the C–O bond was calculated to be 0.279 Å for the substitutions. The axial C–C bonds, i.e., C_1–C_6 and C_1–C_7, also change with substitution. The maximum variation of the C–C bond however, is one order smaller than that of the C–O bond: namely, 0.038 Å. It is noted that the variations of the other bonds were less than 0.048 Å.

Figure 3 shows the relationship between the axial C–C and equatorial C–O distances in **X1**–**X14**. The C–C and C–O bond distances in each compound used in Figure 3 are average values for C_1–C_6 and C_1–C_7 and those for C_1–O_2, C_1–O_3, C_1–O_4, and C_1–O_5, respectively. It should be noted that the individual values are close to each other because of the quasi high symmetry in each compound.

The minimum and maximum C–C distances in Figure 3 are 1.338 and 1.376 Å for **X1** and **X14**, respectively. Based on the concept of Hammett's σ_p, there is a trend that the axial C–C bonds are elongated for the electron-withdrawing rather than the electron-donating groups. Strictly, the order partly replaces each other. It is notable that the compound **X6**, that is, X = H, has a longer C–C distance than those in **X7**, **X8**, **X10**, and **X11**. On the contrary, the minimum and maximum C–O distances are 2.445 and 2.724 Å for **X14** and **X1**, respectively.

As in the case of the C–C bond distances, there is a correlation between the C–O distances and the electron-donating (withdrawing) ability of substituent X: The C–O distances are shorter for the electron-withdrawing groups. As a consequence, a linear correlation is established between the C–C and C–O distances: The longer the C–C distance, the shorter the C–O distance. Therefore, X = NO_2 is the most preferable substitution to create the strongest C–O hypervalent bond among 14 functional groups.

Figure 4 shows the relationship between the C–C and C–O bond energies, which are the average values for C_1–C_6 and C_1–C_7 and those for C_1–O_2, C_1–O_3, C_1–O_4, and C_1–O_5, respectively. Each bond energy is estimated by Bond-EDA. Numer-

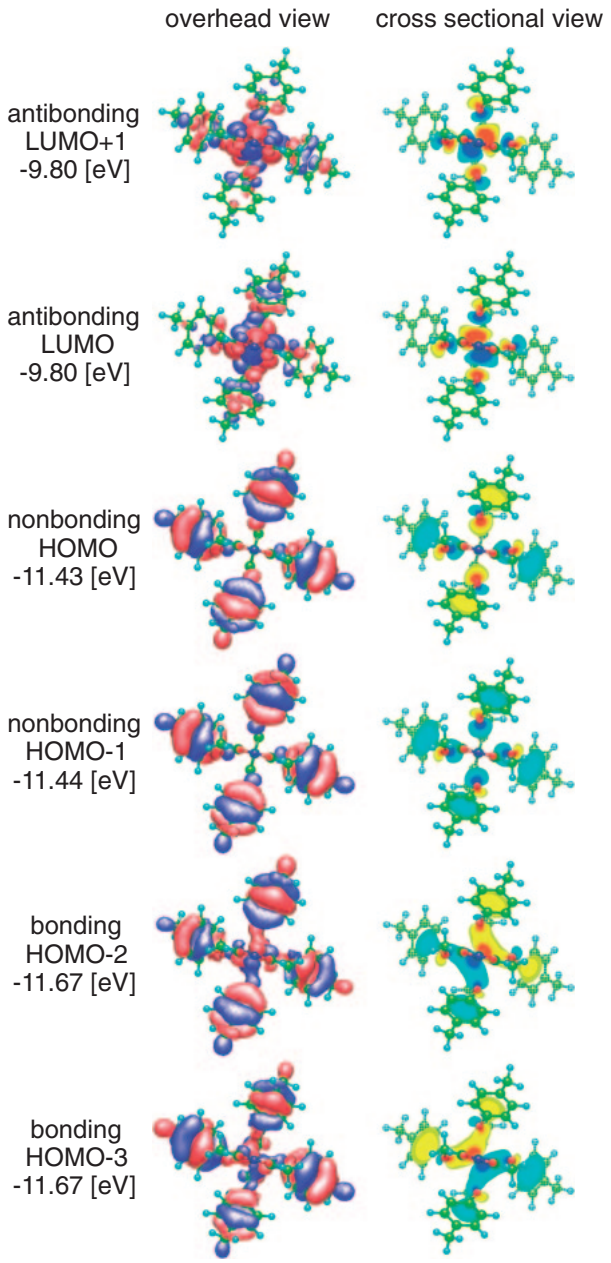


Figure 2. MOs maps regarding the hypervalent O–C–O bond in **X14**.

ical data regarding Figure 4 are given in the Supporting Information. The C–C bond energies of **X1** to **X14** are in the range of 193.6 to 218.2 kcal mol^{-1}, which are close to that of ethylene estimated by Bond-EDA at the B3LYP/cc-pVDZ level: that is, 212.1 kcal mol^{-1}.[10] Roughly speaking, with stronger electron-donating groups, the C–C bond energy becomes smaller. The order however, replaces more frequently than that in Figure 3.

The C–O bond energies are in the range of 13.9 to 23.1 kcal mol^{-1}, which are remarkably smaller than the covalent bond energy. Note that these values are comparable with the hypervalent bond energies in pentacoordinate carbon compounds.[10] A quasi-linear correlation between the C–C and C–O bond energies can be observed. The linearity in Figure 4 is

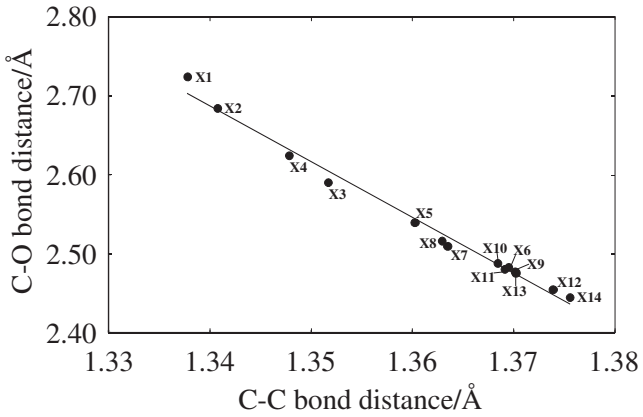


Figure 3. Relationship between C–C and C–O bond distances (in Å) in compounds **X1**–**X14**.

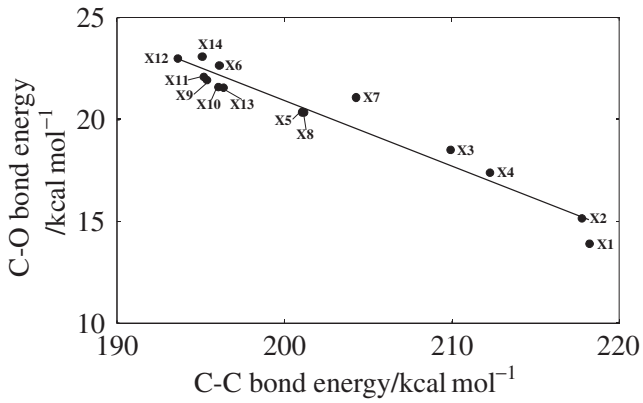


Figure 4. Relationship between C–C and C–O bond energies (in kcal mol^{-1}) in compounds **X1**–**X14**.

slightly worse than that in Figure 3: namely, the coefficients of determination (R^2 values) are 0.9434 and 0.9886, respectively. It indicates that the bond energy is affected not only by the geometric effects but also by the other effects such as electronics.

Next we investigate the substituent effect at the Y position. While the geometric changes are smaller than those for the X substitution, the relationship between the axial C–C and equatorial C–O distances is examined in Figure 5. Note that the bond distances for C_1–C_6 and C_1–C_7 and those for C_1–O_2, C_1–O_3, C_1–O_4, and C_1–O_5 are identical, respectively, because all compounds **Y1**–**Y14** have S_4 symmetry. The C–C and C–O distances are in the ranges of 1.363–1.370 and 2.483–2.527 Å, respectively. There is no apparent correlation between these distances. Careful observation of the data for **Y1**–**Y5** reveals that the C–O distance slightly increases and the C–C distance decreases a little bit with stronger electron-donating substituents. Similarly, the substitution of the stronger electron-withdrawing group from **Y7** to **Y14** leads to somewhat of an increase in the C–O distance and to a modest decrease the C–C distance. The results exhibit the complex substituent effect at the Y position: namely, both electron-donating and -withdrawing groups weaken the C–O bond. As a consequence, Y = H is expected to be the most preferable substitution for a stronger C–O bond.

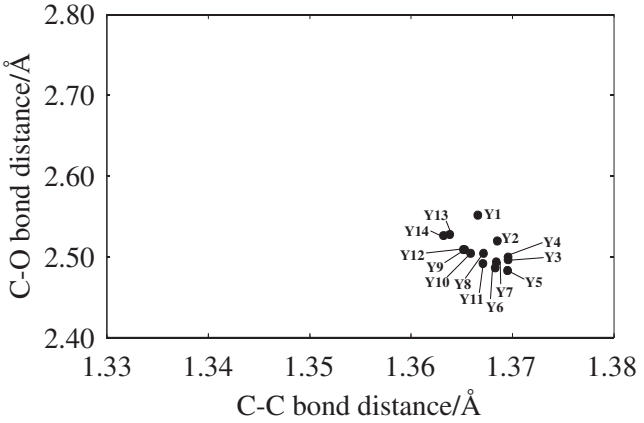


Figure 5. Relationship between C–C and C–O bond distances (in Å) in compounds **Y1**–**Y14**.

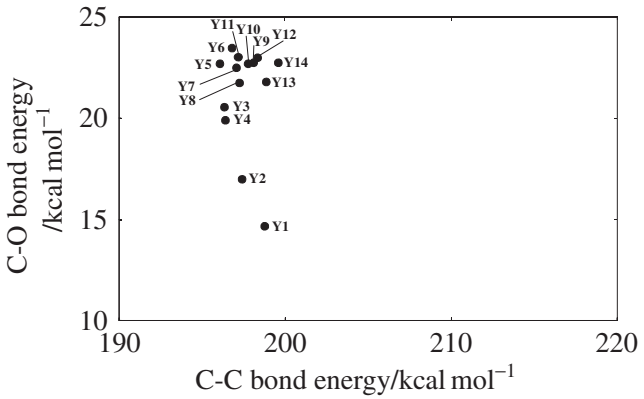


Figure 6. Relationship between C–C and C–O bond energies (in kcal mol^{-1}) of compounds **Y1**–**Y14**.

Figure 6 shows the relationship between the C–C and C–O bond energies in **Y1**–**Y14**. Although the C–C bond energy changes only from 196.1 to 199.6 kcal mol^{-1}, the C–O bond energy varies from 14.7 to 23.5 kcal mol^{-1}. As in the case of the bond distances in Figure 5, it is difficult to find an apparent correlation between them. The C–O bond energy decreases from **Y6** to **Y1** except for the order between **Y4** and **Y3**. On the other hand, the changes from **Y6** to **Y14** are small. Therefore, it is concluded that the effect of the electron-donating groups to the C–O bond energy is larger than that of the electron-withdrawing groups for the substitution at the Y position.

The substitution of X affects the C–C double bonds significantly, while the hypervalent C–O bonds are affected indirectly through sharing the $2p_x$ and $2p_y$ electrons of the central C atom. Consequently, there exist clear correlations between the C–C and C–O bond energies and between those bond distances. On the other hand, the substitution effect of Y, which is the para position of the hypervalent C–O bonds, does not appear in the C–C double bonds.

From theoretical considerations, the substitution of X = NO_2 and Y = H is expected to give the strongest hypervalent C–O interaction. We further performed DFT calculations at the B3LYP/cc-pVDZ level to get the geometry and bond energies of **7**, which is identical to the compound with X = NO_2 and Y = H in **6**. Table 2 summarizes the geometric parameters and

Table 2. Geometric Parameters and Bond Energies in **7**

	Bond distance /Å	Bond angle /degree	Bond energy /kcal mol^{-1}
C_1–O_2	2.438		24.9
C_1–O_3	2.438		24.9
C_1–O_4	2.438		24.9
C_1–O_5	2.438		24.9
C_1–C_6	1.376		194.9
C_1–C_7	1.376		194.9
O_2–C_1–O_4		176.2	
O_3–C_1–O_5		176.2	
C_6–C_1–C_7		180.0	
O_2–C_1–O_3		90.1	
O_2–C_1–C_6		88.1	

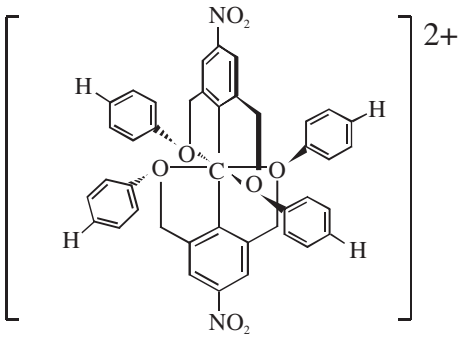


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Chart 3.

bond energies regarding the hexacoordinate hypervalent carbon. Detailed geometry is given in the Supporting Information. As expected, compound **7** (Chart 3) has shorter C–O distances and larger C–O bond energies than those in the other compounds, **X1**–**X14** and **Y1**–**Y14**.

Concluding Remarks

The present study investigated the substituent effects in compound **5**, which was theoretically proposed as an ideal hexacoordinate hypervalent carbon compound in our previous study.[10] The substitutions were performed at the X and Y positions in **6** shown in Figure 1, which correspond to the para positions of the axial C–C and equatorial C–O bonds, respectively. 14 Functional groups shown in Table 1 were investigated. The DFT calculations at the B3LYP/cc-pVDZ level demonstrated that all the derivatives have stable hexacoordinate structures. For substitution at X, it was clarified that both bond distances and bond energies show approximately linear correlations between the axial C–C and equatorial C–O bonds. Namely, with greater electron-withdrawing groups, the hypervalent C–O bonds become strengthened. On the other hand, no apparent correlation between the C–C and C–O bonds could be found for substitution at Y. Careful observation revealed that the substitutions using both electron-withdrawing and -donating groups slightly weaken the hypervalent bond in comparison with hydrogen. Based on the present analysis of the substituent effect, we have theoretically designed the most

favorable hexacoordinate hypervalent carbon compound **7**, that is, X = NO_2 and Y = H.

It is notable that the present calculation to get a better compound is opposite to the experimental approach. Namely, the group of Akiba and Yamamoto tried to introduce an electron-donating substituent as X, whereas the present study suggests an electron-withdrawing substituent as a good candidate. As easily expected, electron-donating substituents stabilize the positive charges of the molecule. However, the 3c-4e bonds, which are necessary to form the hypervalent compound, would be weakened by electron-donating substituents. This reflects the trade-off between the stability of the molecule and formation of a distinct hypervalent bond.

Finally, we should mention that the present theoretical design concentrates on the chemical bond possessing the hexacoordinate carbon compound. The reactivity and the synthesis of the compound remain unknown. For example, NO_2, as seen in **7**, generally exhibits high reactivity. From the viewpoint of the stability of compound, **X13** (X = CN, Y = Me) may be an alternative candidate. However, we believe that our theoretical design would help future experimental study for challenging the hexacoordinate carbon compound.

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Supporting Information

Geometric parameters and summary of frequency analyses of **X1**–**X14** and **Y1**–**Y14** (**X6** = **Y5**), MOs for the 3c-4e bond in **X2**–**X13** and **Y1**–**Y14**, numerical data regarding Figures 3–6, and geometric parameters of **7** are available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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