

Frontier Orbitals of Fifteen $C_{20}H_{17}(OH)_3$ Regioisomers: Hybrid DFT B3LYP Study

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The hybrid density-functional (B3LYP/6-31G(d,p)) method was used to analyze the substitution effect on the $C_{20}H_{20}$ cage based on calculation of the frontier orbitals of fifteen $C_{20}H_{17}(OH)_3$ derivatives. All substitution products were geometrically optimized without constraints and confirmed by frequency analysis. The results suggest that the *cis*-1 *cis*-1 *cis*-2 regioisomer is the most stable isomer, which implies that hydrogen bonding exerts a stronger effect on the relative energies of the trihydroxide than long-range interactions. Thus, this supports the experimental result in which the bisvicinal tetrol was of particular preparative-synthetic interest. While the LUMO of each of the $C_{20}H_{17}(OH)_3$ regioisomers was equivalently delocalized over the void within the cage, the HOMO was limitedly delocalized on substituents and carbons in close proximity to the substituents. The characteristics of the HOMO of each of the regioisomers vary based on the substitution sites. This indicates that the 15 regioisomers of each $C_{20}H_{20}$ trisubstituted derivative might undergo an entirely different set of characteristic chemical reactions with electrophilic reagents. The results further suggest that the penta-substituted OH groups on the surface of the fullerene cage are more likely to be localized on a pentagon than to be homogeneously delocalized.

Key Words : $C_{20}H_{17}(OH)_3$ regioisomers, Hybrid density-functional (B3LYP) calculations, Frontier orbitals, HOMO and LUMO

Introduction

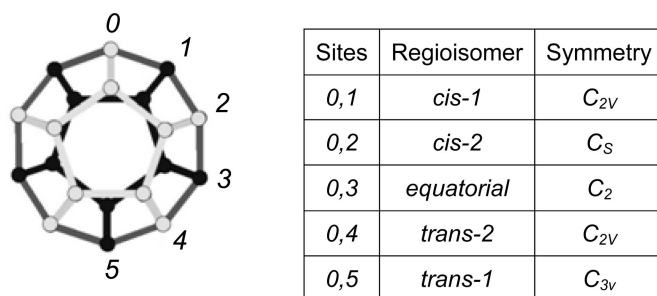
The isolated-pentagon rule (IPR) states that the most stable fullerenes are those in which all pentagons are located as far as possible from one another and are surrounded by five hexagons.^{1,2} However, the IPR rule cannot be satisfied for the smallest fullerene.³ This non-IPR fullerene is necessarily highly reactive owing to the fusion of the strained 5-membered rings (MRs). Thus the formation of $C_{20}H_{20}$ through sp^3 -bond-forming reactions and a modification of the structural and electronic properties of $C_{20}H_{20}$ should be of interest to both experimentalists and theoreticians because the small fullerene cage may be a candidate molecule for fabrication of molecular single solvated electron system.

Moreover, isomerism is a fundamental concept in chemistry, where the term "regioisomer" refers to a type of structural isomer. In the formation of regioisomers, regioselectivity is observed in the chemical reactions of molecules with different orientations or reaction sites. Although the regioisomers of fullerenes with 5- and 6-MRs have been extensively studied,^{4,5} similar evaluations of the regioisomers of $C_{20}H_{20}$ fullerene derivatives containing only 5-MRs have been sparse. Empirical investigation of polysubstituted $C_{20}H_{20}$ has been reported,^{6,7} with different substituents (X), including OH, F, Cl, Br, and CO_2CH_3 . By using force-field calculations for $C_{20}H_{20}$, the molecular strain associated with increasing functionalization of $C_{20}H_{20}$ with increasingly more voluminous substituents has been analyzed.⁷ The derived MM2 strain energies suggest that 1,2-dihydroxy dodecahedrane

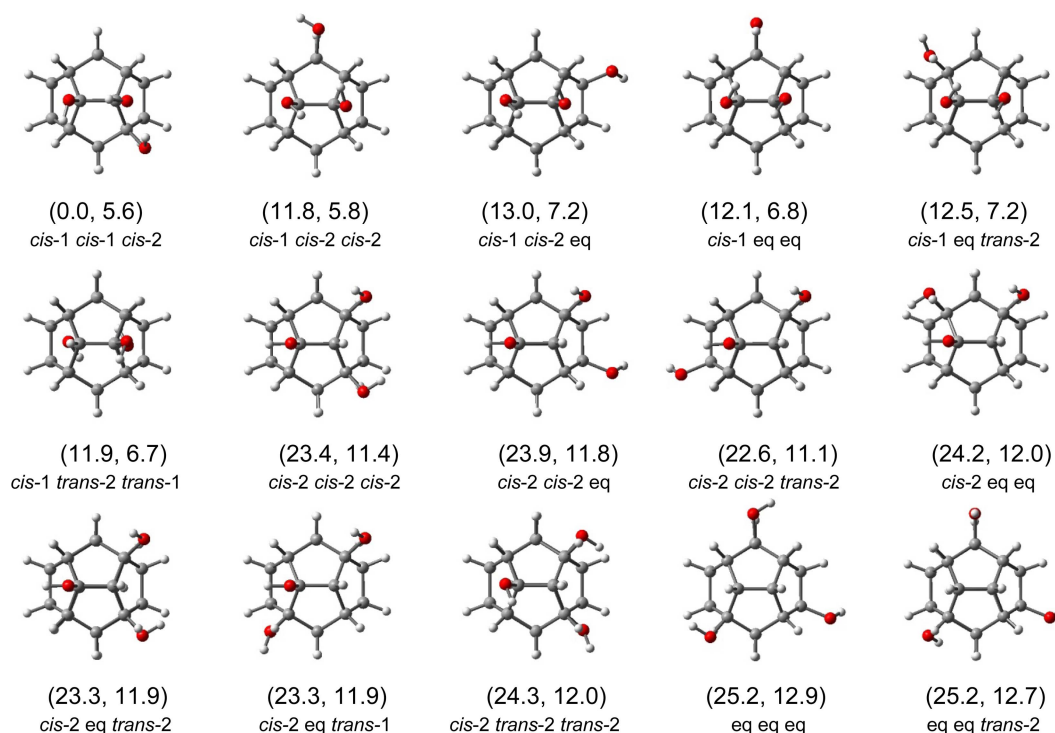
(vicinal OH, *cis*-1) is more strained than the 1,3-dihydroxy (*cis*-2) counterpart. Proton transfer between the -OH groups of two $C_{20}(OH)_2$ molecules has previously been examined by means of *ab initio* molecular orbital calculations.⁸ Hydrogenated carbon fullerenes have been studied at the B3LYP level of theory.⁹

Based on our previous analysis of $C_{20}H_{18}X_2$ regioisomers (X = F, Cl, Br, or OH) using hybrid B3LYP//6-31G(d,p) DFT calculations, the relative energies were found to increase in an order that is different to the increasing order of strain energies.¹⁰ Of the five hydroxy substituted regioisomers, vicinal substitution produces the highest strain energy, but the lowest relative energy in terms of total energy.

Recently, the planarity of benzene was analyzed *via* various theoretical methods, and the B3LYP/6-31G(d) calculation was found to be suitable for simulating the experimentally determined structure of benzene.¹¹ A number of theoretical studies on the parent C_{20} cage⁹ as well as $C_{20}H_{20}$ dodecahedrane,¹² $C_{20}F_{20}$ perfluorododecahedrane forming the solvated electron system,^{13,14} and $C_{20}X_2$ and $C_{20}H_{18}X_2$ regioisomers (X = H, F, Cl, Br, and OH),^{10,15} have been reported. To the best of our knowledge, calculations of the full optimization of 15 trisubstituted $C_{20}H_{17}(OH)_3$ regioisomers at the B3LYP/6-31G(d,p) level have not yet been reported. Therefore, in this study, 15 regioisomers of the $C_{20}H_{17}(OH)_3$ derivative cage obtained by full geometry optimization were considered. Determination of the relative energies, electronic properties, and atomic structures of $C_{20}H_{17}(OH)_3$ regioisomers having the same spin state is presented herein. Even though the predominant electronic configurations of the LUMO of



(a) Nomenclature of regioisomers based on relative positions of two substituents on $C_{20}H_{20}$ cage (hydrogen atoms deleted for clarity of carbon numbering).



(b) Atomic structures of 15 trisubstituted $C_{20}H_{17}(OH)_3$ cage regioisomers. The relative and strain energies (kJ/mol) of each regioisomer are presented in parentheses.

Figure 1. (a) Nomenclature of regioisomers based on relative positions of two substituents on $C_{20}H_{20}$ cage. Hydrogen atoms are omitted to enable clear imaging of the carbon numbering scheme used to distinguish the different substituent sites. (b) Atomic structures of 15 trisubstituted $C_{20}H_{17}(OH)_3$ cage regioisomers; the relative and strain energies are presented in parentheses for each regioisomer. The relative energy of each regioisomer is the energy minus the lowest energy among the regioisomers. Here the energy of each regioisomer is corrected with the zero-point energy.

the 15 regioisomers are similar, the HOMO maps differ for the various regioisomers. This suggests that the various exohedral complexes may undergo a distinct set of characteristic chemical reactions with electrophiles.

Calculations

Hybrid density-functional theory (DFT) with Becke's three-parameter hybrid method and the Lee-Yang-Parr exchange-correlation functional theory (B3LYP)¹⁶⁻¹⁸ were used to optimize the geometries of the $C_{20}H_{17}(OH)_3$ regioisomers. The electron basis set of 6-31G(d,p) was used in this study.¹⁹

The geometries of all the $C_{20}H_{17}(OH)_3$ regioisomers were fully optimized using the Gaussian 2003 B.04 package suite.²⁰ The convergence criterion with tight optimization and an ultrafine pruned (99,590) grid (using the keywords Opt = Tight, Grid = ultrafine) were utilized in order to obtain highly-accurate geometries and frequencies. The relative energies, strain energies, and the HOMO and LUMO orbitals of the regioisomers were analyzed.²¹

Here, the strain energy was calculated on the basis of the energy difference between the single point energies of the $C_{20}H_{17}$ fragment of optimized $C_{20}H_{17}(OH)_3$ and the $C_{20}H_{17}$ fragment of optimized $C_{20}H_{20}$.

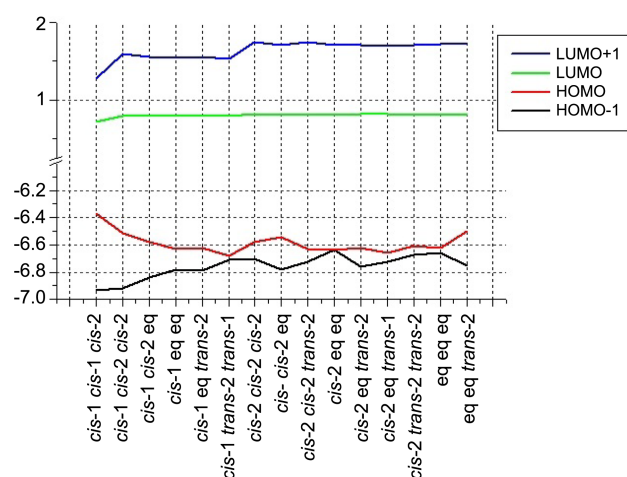


Figure 2. The HOMO-1, HOMO, LUMO, and LUMO+1 energy levels (eV) of 15 $C_{20}H_{17}(OH)_3$ regioisomers calculated at the B3LYP/6-31G(d, p) level. The HOMO and LUMO energy levels (eV) of $C_{20}H_{20}$ at the same level of theory are -7.09 and 0.90 , respectively.

Results and Discussion

The relative and strain energies (kJ/mol) of 15 regioisomers were determined based on full optimization calculations of the atomic structures of the $C_{20}H_{17}(OH)_3$ regioisomers at the B3LYP/6-31G(d, p) level without any constraints under the reinforced tight convergence criterion, the approximate symmetries of which were: C_{3v} (*cis-2 cis-2 cis-2*; eq eq eq), C_s (*cis-1 cis-1 cis-2*; *cis-1 cis-2 cis-2*; *cis-1 eq eq*; *cis-1 trans-2 trans-1*; *cis-2 cis-2 trans-2*; *cis-2 eq eq*; *cis-2 trans-2 trans-2*; eq eq *trans-2*), C_1 (*cis-1 cis-2 eq*; *cis-1 eq trans-2*; *cis-2 cis-2 eq*; *cis-2 eq trans-2*; *cis-2 eq trans-1*), as shown in Figure 1. The cutoffs on the forces and step size were reduced by the pruned (99,590) grid (keywords Opt = Tight, Grid = ultrafine), which was used to obtain accurate geometries. The local ground states of these structures were confirmed by using the frequency analysis. Of the 15 regioisomers that were fully geometrically optimized, the relative energies of the trihydroxide derivatives were found to be dependent on the distance between two hydroxyl groups, but independent of the symmetry.

Here, we analyzed the effect of the trisubstituents on the strain in the most-stable cage of neutral $C_{20}H_{20}$ with I_h symmetry (the calculated C-C bond length was 1.556 \AA , which is within the range of the corrected experimental result²² of $1.555 \pm 0.005 \text{ \AA}$), and the strain energies of the regioisomers of each $C_{20}H_{17}(OH)_3$ derivative were also determined as shown in Figure 1. Further, the energy levels and the orbital maps of the HOMO-1, the HOMO, the LUMO, and the LUMO+1 of the regioisomers of the 15 different $C_{20}H_{17}(OH)_3$ derivatives are shown in Figures 2 and 3, respectively.

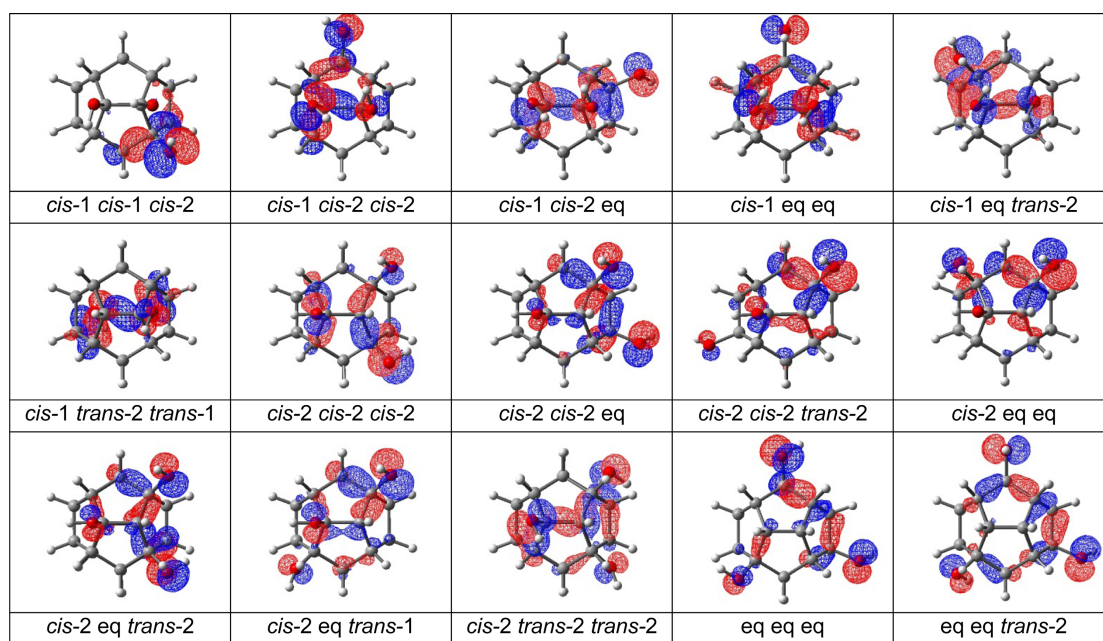
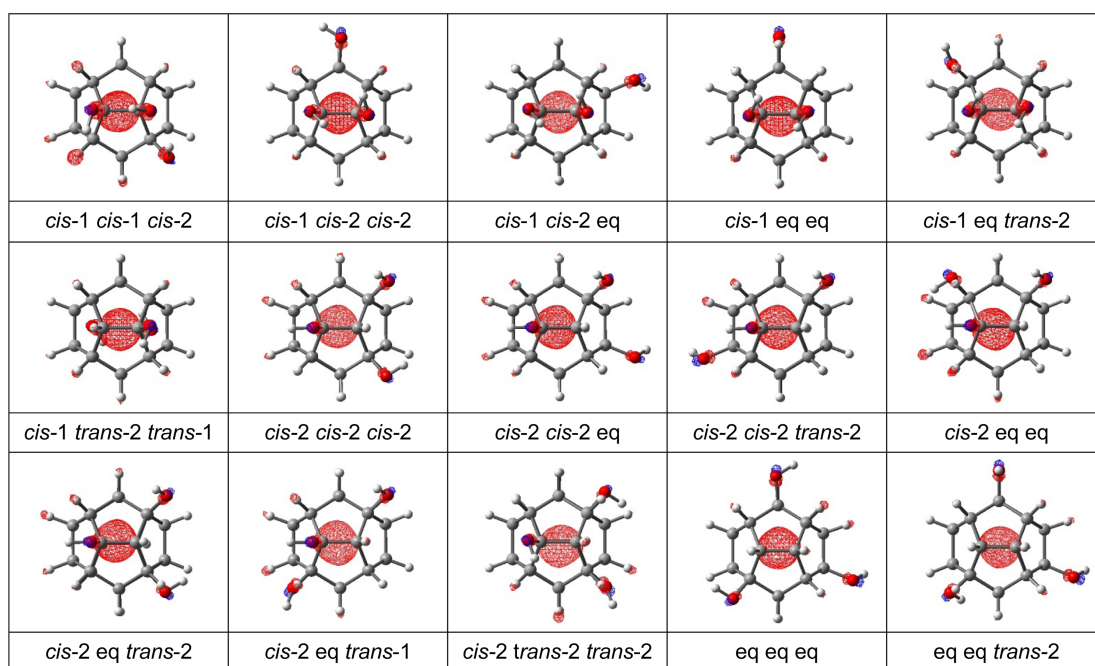
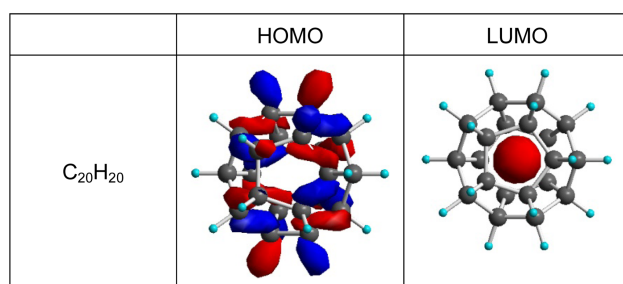
The relative energies of the dihalo dodecahedranes increased in the order *trans-1* (D_{3d}) < *trans-2* (C_{2v}) < *equatorial* (C_2) < *cis-2* (C_s) < *cis-1* (C_{2v}),¹⁰ and in the case of $C_{20}X_2$ ($X = F, Cl, Br$), the *cis-1* isomers had the lowest energy and *trans-1* isomers had the highest energy.¹⁵ In contrast, the relative

energies of the regioisomers of the dihydroxy derivatives increased in the order *cis-1* (C_{2v}) < *cis-2* (C_s) < *equatorial* (C_2) < *trans-2* (C_{2v}) < *trans-1* (D_{3d}); i.e., the relative energies were proportional to the strength of the hydrogen bonds between the two hydroxyl groups.¹⁰ It was found herein that the relative energies of the regioisomers containing *cis-1* substituents were lower than those of the other isomers, the relative energy of the *cis-1 cis-1 cis-2* regioisomer being the lowest, which is consistent with experimental data for the vicinal diol *cis-1* regioisomer of dihydroxy dodecahedrane.⁷

The calculated results demonstrated that the strain energy increased in response to the addition of OH groups in all 15 regioisomers relative to the strain energy of $C_{20}H_{20}$. However, among the evaluated regioisomers, those with *cis-1* substituents exhibited relatively lower strain energy. Further, it is interesting that the *cis-1 cis-1 cis-2* regioisomer of the $C_{20}H_{17}(OH)_3$ cage with C_s symmetry had the lowest energy, indicative of strong hydrogen bonds between the two hydroxyl groups. The smallest cage strain was found for the *cis-1 cis-1 cis-2* regioisomer of the $C_{20}H_{17}(OH)_3$ cage. Figure 1 shows the strain energies, illustrating that the relative energy of the regioisomers with *cis-1* substituents were generally lower than that of the other isomers. Here the coefficient of determination between the relative energy and the strain energy is 0.9, implying that 90% of the total variation in the relative energy can be explained by the linear relationship between the relative energy and the strain energy (as described by the regression equation).

Thus, our model calculations for the deformed cages of the $C_{20}H_{17}(OH)_3$ regioisomers indicate that the dispersion interaction in trihydroxyl substitutions exerts a weaker influence on the energy than the deformation strain of the unsubstituted cage. Therefore, the hydrogen bonds formed by trihydroxyl substitution are the strongest factors affecting the relative stability of the trisubstituted cage (see Figure 1). The energy gaps of the HOMO-1, the HOMO, the LUMO, and the LUMO+1 energy levels of the regioisomers are shown in Figure 2, illustrating the difference in the energy gaps of the $C_{20}H_{20}$ and $C_{20}H_{17}(OH)_3$ cages. Here we see that the contribution to release the strain of the regioisomers would be due to the energy level of the HOMO-1 more than that of the HOMO.

Figures 3 shows the HOMOs and LUMOs of the regioisomers of the $C_{20}H_{17}(OH)_3$ trisubstituted cages, illustrating the effect of the trisubstituents on the frontier orbitals of $C_{20}H_{20}$. The frontier orbitals are very useful to visualize the regions of electron "localization" and possible functionalization, as well as for expected possible chemical similarities, when they would not give the additional quantitative information.⁹ Although the HOMO maps of the regioisomers with different geometric structures are different, the LUMOs of the $C_{20}H_{17}(OH)_3$ -trisubstituted regioisomers are similar. While the LUMO of each of the $C_{20}H_{17}(OH)_3$ regioisomers was equivalently delocalized over the void within the cage, the HOMO was limitedly delocalized on substituents and carbons in close proximity to the substituents. This suggests that each of the regioisomers should undergo a distinct set of

(a) The HOMOs of 15 $C_{20}H_{17}(OH)_3$ regioisomers (isovalue = 0.05).(b) The LUMOs of $C_{20}H_{17}(OH)_3$ regioisomers (isovalue = 0.05).(c) The HOMO and LUMO of the $C_{20}H_{20}$ cage (isovalue = 0.05).**Figure 3.** The HOMOs (a) and LUMOs (b) of fully optimized geometries of 15 $C_{20}H_{17}(OH)_3$ regioisomers at the B3LYP/6-31G(d, p) level; The HOMO and LUMO (c) of $C_{20}H_{20}$ cage at the B3LYP/6-31G(d, p) level.

characteristic chemical reactions with electrophiles. The HOMO energies of the $C_{20}H_{17}(OH)_3$ regioisomers were increased relative to the HOMO of $C_{20}H_{20}$, whereas the LUMO energy levels of all of the regioisomers were lower than that of $C_{20}H_{20}$ (HOMO: -7.09 eV; LUMO: 0.90 eV). But, the band gaps of the regioisomers were wider than that of C_{20} (HOMO: -5.03 eV; LUMO: -3.10 eV) were narrower than that of $C_{20}H_{20}$. Given that the LUMO energies of the evaluated regioisomers were all slightly lower than that of $C_{20}H_{20}$, it is implicit that these species are slightly stronger electron acceptors than $C_{20}H_{20}$. Here the HOMO-LUMO gaps are considered as a measure of kinetic stability for regioisomers. Thus the *cis*-1 *cis*-1 *cis*-2 isomer has the lowest total energy, but has the lowest HOMO-LUMO energy gap, implying that it has the worst kinetic stability.

Conclusion

The geometries of 15 regioisomers of the $C_{20}H_{17}(OH)_3$ cage (the smallest trisubstituted fullerene) were fully optimized without any constraint at the B3LYP/6-31G(d) level of hybrid B3LYP density-functional theory. The relative energies of the $C_{20}H_{20}$ trisubstituted regioisomers were found to depend primarily on hydrogen bonding between two of the substituents. Therefore, it is interesting that the regioisomer with a higher number *cis*-1 disubstituents is more stable than the others, as in the case of the dihydroxy derivatives in which the *cis*-1 regioisomer was found to be more stable than the *trans*-1 regioisomer. In the trihydroxides, the effect of the hydrogen bonds is stronger than the strain effect. Here, increased vicinal substitutions lower the energy of the trihydroxide. Thus, this supports the experimental report in which the bisvicinal tetrol was found to be a viable substitute for the lacking bisvicinal tetrabromide in synthetic studies.^{7,23}

The HOMO maps of the 15 evaluated regioisomers of the $C_{20}H_{17}(OH)_3$ cage were found to differ, whereas the LUMO maps were essentially similar. Further, the HOMO distribution of each of the $C_{20}H_{17}(OH)_3$ regioisomers differed independent of the symmetry, whereas the LUMO distributions were almost the same. This suggests that the 15 regioisomers of the $C_{20}H_{20}$ trisubstituted derivatives should undergo entirely different sets of characteristic chemical reactions with electrophiles, which may be verified empirically.

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Supporting Information. The atomic structural data of 15 regioisomers of the $C_{20}H_{20}$ trisubstituted derivatives is available.

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