Flat building blocks for flat silicene

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Silicene is the silicon equivalent of graphene, which is composed of a honeycomb carbon structure with one atom thickness and has attractive characteristics of a perfect two-dimensional $\pi$-conjugated sheet. However, unlike flat and highly stable graphene, silicene is relatively sticky and unstable due to its puckered or crinkled structure. Flatness is important for stability, and to obtain perfect $\pi$-conjugation, electron-donating atoms and molecules should not interact with the $\pi$ electrons. The structural differences between silicene and graphene result from the differences in their building blocks, flat benzene and chair-form hexasilabenzene. It is crucial to design flat building blocks for silicene with no interactions between the electron donor and $\pi$-orbitals. Here, we report the successful design of such building blocks with the aid of density functional theory calculations. Our fundamental concept is to attach substituents that have $sp$-hybrid orbitals and act as electron donors in a manner that it does not interact with the $\pi$ orbitals. The honeycomb silicon molecule with BeH at the edge designed according to our concept, clearly shows the same structural, charge distribution and molecular orbital characteristics as the corresponding carbon-based molecule.

Silicene is the silicon equivalent of graphene, which is a famous material composed of a honeycomb layer of carbon just one atom thick. If applied to electronic devices, these silicene layers would enable the semiconductor industry to achieve ultimate miniaturization. However, unlike flat and highly stable graphene, silicene is relatively sticky and unstable due to its puckered or crinkled structure. To produce silicene, the hot vapor of silicon atoms is condensed onto crystalline blocks of silver or other materials. However, the substrate can affect the $\pi$-conjugated system. Recent twisted silicene multilayers have proved the two-dimensional (2D) nature of silicene and was a major progress toward flat silicene, but interlayer interactions still perturb the electronic structure of 2D materials.

The building blocks of graphene are benzene and/or C6 clusters, both of which are flat. Benzene is an archetypical aromatic hexagon composed of carbon with delocalized $\pi$ electrons. The 2D aromaticity of flat monocyclic systems is governed by the Hückel $4N+2$ rule, where $N$ is the number of $\pi$ electrons. The outstanding properties of C6 clusters include double aromaticity with an orthogonal Hückel framework (an out-of-plane $p_z$ orbital and an in-plane radial-type orbital contributing to $\sigma$-aromaticity in a single molecule). We previously discovered a similar flat silicon hexagon with double aromaticity, i.e., the dianion of the Si6 cluster (Fig. 1d). This finding encouraged us to design the present flat silicene building blocks using electron-donating substituents. A pioneering work recently reported the formation of flat silicene via doping with calcium as an electron donor, and attempts to make flat hexasilabenzene and Si6 clusters were carried out earlier with Zintl anions. In either case, the Si6 hexagon is surrounded by an electron donor, creating a three-dimensional crystal but not a pure 2D crystal.

To realize a perfect and stable $\pi$-conjugated 2D sheet of silicene, the sheet must be flat and have no electron-donating atoms or molecules interacting with the $\pi$ electrons. The only way to donate electrons without disturbing the out-of-plane $\pi$ orbital is to modify the in-plane edges. A theoretical study of silicene molecules (large polycyclic molecules consisting of six-membered silicon rings) from Si6H9 to Si60H24 showed that silicene molecules with hydrogen atoms at the edge are not flat but have a low-buckled structure. This indicates that, as described above, electron-donating substituents are good candidates for the formation of flat silicene molecules and hydrogen atoms are not suitable. Although a theoretical attempt to use an electron-donating metal, such as lithium, at the in-plane edge gave the $D_{6h}$ planar structure of hexasilabenzene, the lithium atoms were not attached to one silicon atom but instead attached between two adjacent silicon atoms due to the ability of silicon to form three-center bonds with lithium. Furthermore, the bicyclic chain is no longer flat when lithium is used as the electron donor but is puckered with a zigzag chain. A completely different concept is necessary for the design of a flat polycyclic molecule consisting of silicon hexagons as flat silicene building blocks. Here, we report the...

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The successful design of flat 2D molecules composed of six-membered silicon rings with modifications at the in-plane edges using density functional theory (DFT) calculations.

Results
Basic concept. Our basic concept for the design of flat polycyclic molecules consisting of silicon hexagons is to use $sp$-hybrid orbitals (Fig. 2b) with electron-donating ability. We first considered the differences between C-H and Si-H interactions. Notably, the energies of the interacting orbitals are different. That is, the energy difference between the H 1s and Si 3p orbital is larger than that between the H 1s and C 2p orbital. The use of a lithium 2s orbital instead of a hydrogen 1s orbital is a straightforward way to compensate for the energy difference (Fig. 2a). However, unlike hydrogen, the empty 2p orbital (Fig. 2b) of lithium interacts with the silicon 3p orbital and forms a three-center bond with two adjacent silicon atoms of the silicon ring. Eventually, we decided to use linear $sp$-hybrid orbitals and selected BeH as the substituent. First-year chemistry textbooks state that BeH$_2$ has a linear shape due to its $sp$-hybrid orbital. Figure 2b shows the molecular orbital of an Li atom and BeH radical for comparison. The difference between the two singly occupied molecular orbitals (SOMOs) is that the SOMO of the BeH radical points to the Si$_6$ ring (Fig. 2b). Silicon equivalents 1, 2, 3, 4 and 5 of benzene (6), naphthalene (7), anthracene (8), pyrene (9) and coronene (10), respectively, were selected as building blocks and substituted with BeH at the ring edge (Fig. 3).

Optimized structure. The five silicon-based molecules 1–5 with BeH at the ring edge show the same structural, charge distribution and molecular orbital features as the corresponding carbon-based molecules 6–10, where BeH is used according to the above concept. All of the calculated molecules 1–10 have a flat structure as their minimum with no imaginary frequencies. Electron donation stabilizes the flat structure of the six-membered silicon ring and further provides the stable flat structure of polycyclic silicon molecules. The lowest
atom is strongly positive (green), while that of the hydrogen in BeH is strongly negative (red). These trends are
strongly negative (red), while that of the silicon inside the ring is nearly neutral (black). The charge of the Be
silicon-based molecules
–1
 distribution in molecules
–1
 negative, indicating electron donation from the terminal BeH to the ring moiety. Figure 4 compares the charge

Table 1. Optimized geometry, charge (Q ring), frequency (ν b)
and HOMO-LUMO gap of molecules 1–10 at the B3LYP/cc-pVTZ level. The notation r 1–r 5 represents the bond length between the X atoms (X = Si, C) shown in Fig. 3. a Q ring: Summation of the NPA charges on the ring. b ν b : The lowest vibrational frequency. c HOMO-
LUMO gap from the first excitation energies obtained by TDDFT/B3LYP. HOMO-LUMO gap from the Kohn-Sham eigenvalues of the ground state DFT/B3LYP calculation is given in parentheses.

vibrational frequency modes (ν b ), given in Table 1, are the out-of-plane motion of the terminal BeH moiety (3) and the out-of-plane ring deformation (1, 2, 4–10), respectively. The calculated silicon-silicon bond length (2.22 to 2.28 Å) is between the silicon-silicon single and double bond length (the bond lengths of H 3Si–SiH 3 and H 2Si–SiH 2 at the B3LYP/cc-pVTZ level are 2.355 Å and 2.166 Å, respectively), which is similar to the structure of aromatic benzene having a bond length between the carbon-carbon single and double bond. The silicon-silicon bond lengths are equal in hexasilabenzene 1 due to its D 6h symmetry but differ at most by 0.06 Å in the other molecules 2–5. The carbon-based structures 6–10 show the same behavior. Benzene 6 has the same carbon-carbon bond lengths throughout the ring, while the others 7–10 have slightly different bond lengths, with the difference being at most 0.08 Å. Notably, the terminal BeH is not located between the two silicon atoms in the minimized structures of 1–5, which is markedly different from the lithium-terminated six-membered ring Si 6Li 6 31.

Charge distribution. As shown in Table 1, the total NPA charges on the silicon rings (Q ring ) of 1–5 are all negative, indicating electron donation from the terminal BeH to the ring moiety. Figure 4 compares the charge distribution in molecules 1–5 to that of 6–10. The charge of the ring-edge silicon, at which BeH is directly bound, is strongly negative (red), while that of the silicon inside the ring is nearly neutral (black). The charge of the Be atom is strongly positive (green), while that of the hydrogen in BeH is strongly negative (red). These trends are the same as those in 6–10, but the contrast between the negative and positive charges is slightly enhanced in the silicon-based molecules 1–5. The total NPA charge on the carbon ring (Q ring ) of 6–10 is negative, and the ring is surrounded by positively charged hydrogen atoms. The edge carbon is negatively charged, and the inside of the ring is nearly neutral. The neutrality of the charge inside the ring is more evident in larger molecules. The charge distribution indicates that BeH terminates the silicon equivalents 1–5 as well as the hydrogen atoms of 6–10.

Molecular orbitals. Pure π-conjugation is a key property of flat silicene as well as flat graphene. The highest
occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are shown in Fig. 5. The HOMO and LUMO of 1–5 are all confirmed to be π orbitals. Their shapes are similar to the HOMO and LUMO of 6–10, but slightly delocalized on the Be atoms. Thus our design using a linear sp-hybrid orbital at
the terminus is expected to successfully provide the building blocks for flat and stable π-conjugated silicene. The HOMO-LUMO gap of all the proposed precursor molecules are listed in Table 1.

Other hexagons and isomers. Several other hexagons X₆R₆ (X = Si, Ge) were calculated to investigate which R substituents, other than Si₆(BeH)₆, can be used for the design of flat hexagons (Table 2). Since our aim is to obtain a six-membered ring with D₆h symmetry, we optimized the structure under the constraint of D₆h symmetry. In case of metal substitution at ring edge, two types of structures have the symmetry of D₆h (Fig. 6): benzene-like (A) and Si₆Li₆-like where metal moves between two silicon atoms (B). For comparison, the results of Si₆H₆ and Si₆Li₆ of structure A at the same level of calculations as our present work are also listed in Table 2. As is well known, our results also showed benzene-like structure of Si₆H₆ and Si₆Li₆ did not give a minimum. Among the optimized hexagons in Table 2, a flat D₆h ring was obtained as the minimum for only the MgH-terminated six-membered silicon ring and the BeH-terminated six-membered germanium ring. In both hexagons, MgH and BeH have an sp-hybrid orbital and acts as an electron donor. In the optimized structure, BeH and MgH do not migrate to between the silicon atoms or germanium atoms. The optimized silicon-silicon and germanium-germanium bond lengths are 2.264 Å and 2.350 Å, respectively. Although the minimized geometry of the MgH-terminated six-membered silicon ring has a flat structure, the planar hexagon is not the minimum of the MgH-terminated six-membered germanium ring but is instead its 1st order transition state (TS). Furthermore, with CaH substitution, both the six-membered silicon and germanium rings become considerably higher order TS. Therefore, light metals are better for the design of flat hexagons. The imaginary mode of MgH-terminated six-membered germanium ring is the out-of-plane motion of MgH, which leads to a nonplanar structure. This motion does not cause MgH to migrate between two germanium atoms. The lowest vibrational frequency of BeH-terminated six-membered germanium ring is 22.24 cm⁻¹, which is much smaller than that of BeH-terminated six-membered silicon ring (47.57 cm⁻¹). This makes it difficult to design flat building blocks for flat germanene. A proper substituent at the ring edge is required to tune the charge on the ring and the bond strength between Ge and the substituent.

Several monovalent and divalent metals with electron-donating ability were examined as substituents (R = Na, K, Mg, Ca, Cu, Zn), but these did not produce flat D₆h hexagons as the minimum. Table 2 lists more stable structure between the two D₆h structures, benzene-like (A) and Si₆Li₆-like (B). Three are 1st order TSs, and the others are higher order TSs. The imaginary modes of the 1st order TSs are the out-of-plane motion of the metal (R = K and Zn) and out-of-plane ring deformation (R = Ca), leading to a nonplanar minimum. As mentioned before, the lithium-terminated six-membered silicon ring has a D₆h planar structure 29–31, and the lithium atom is not attached to one silicon but between two adjacent silicon atoms. Cu showed a benzene-like structure (A), while the other metals migrated between two silicon atoms (B) similar to lithium. Thus, simple electron donation is insufficient for the design of flat hexagons. Next, for the substituent with an sp-hybrid orbital (R = C≡N), the D₆h structure was obtained as the 1st order TS. The imaginary mode is out-of-plane ring deformation, leading to a nonplanar minimum. Therefore, a simple sp-hybrid orbital without electron donation is also insufficient for the design of flat hexagons.

Figure 4. Charge distribution of molecules 1–10. Each atom is colored according to the charge, and the number indicates the charge.
Hexasilabenzene is known to be less stable than many of its isomers. For example, synthetically accessible hexasilaprismane is more energetically stable. To examine the relative stability between the isomers of our system, we calculated the six valence isomers of Si6(BeH)6 and obtained the silicon equivalent of benzvalene, prismane and bicyclopropenyl in addition to benzene as a minimum. Among the four, BeH-terminated hexasilabenzene is the most stable at the B3LYP/cc-pVTZ level of calculation. Since BeH-terminated hexasilabenzene is not the most stable isomer, the step-by-step manufacture of flat silicene from BeH-terminated hexasilabenzene is not recommended. It would be better to prepare zigzag silicene and then terminate it with BeH.

Figure 5. HOMO and LUMO of molecules 1–10. The molecular orbitals were calculated at the B3LYP/cc-pVTZ level and are depicted at the 0.01 and 0.02 isovales for 1–5 and 6–10, respectively.

| X | R   | Stationary point | Imaginary Mode of 1st TS | Structure |
|---|------|------------------|--------------------------|-----------|
| Si | Na   | 3rd TS           | Out-of-plane motion of K  | B         |
| Si | K    | 1st TS           | Out-of-plane ring deformation | A         |
| Si | Mg   | 2nd TS           | Out-of-plane motion of MgH | A         |
| Si | Ca   | 6th TS           | Out-of-plane ring deformation | A         |
| Si | C≡N  | 1st TS           | Out-of-plane ring deformation | A         |
| Si | MgH  | MIN              |                          | A         |
| Si | CaH  | 6th TS           |                          | A         |
| Ge | BeH  | MIN              |                          | A         |
| Ge | MgH  | 1st TS           | Out-of-plane motion of MgH | A         |
| Ge | CaH  | 17th TS          |                          | A         |
| Si | H    | 1st TS           | Out-of-plane ring deformation | A         |
| Si | Li   | 6th TS           |                          | A         |

Table 2. Optimized hexagonsXRR with D6h symmetry. Full geometry optimizations were performed at the B3LYP/6-311++G(3df,3pd) level for K, Ca, Cu, Zn and CaH substitution, and at the B3LYP/cc-pVTZ level for H, Li, Na, Mg, C≡N, BeH and MgH substitution. aMIN: minimum, TS: transition state. bTwo D6h structures A and B are shown in Fig. 6. More stable structure between the two D6h structures is listed for the terminal substituent of metals (R = Na, K, Mg, Ca, Cu, Zn). For comparison, the results of Si6H6 and Si6Li6 of structure A are listed.
To investigate the charge at each atom, natural population analysis (NPA)51–56 charges were calculated, as NPA parameters were fully optimized, and the minimized structures were confirmed to have no imaginary frequencies.

Gao, J. & Zhao, J. Initial geometries, interaction mechanism and high stability of silicene on Ag(111) surface.

Feng, B.

Brumfiel, G. Sticky problem snares wonder material.

Tao, L.

Vogt, P. et al. Silicene: Recent theoretical advances.

Zhao, J.

Peplow, M. Silicene makes its transistor debut.

Guzmán-Verri, G. G. & Voon, L. C. L. Y. Electronic structure of silicon-based nanostructures.

Vogt, P.

Kaltsas, D., Tsetseris, L. & Dimoulas, A. Structural evolution of single-layer films during deposition of silicon on silver: A first-principles study. J. Phys.: Condens. Matter 24, 442001, doi:10.1088/0953-8984/24/44/442001 (2012).

Guo, Z.-X., Furuya, S., Iwata, J.-I. & Oshiyama, A. Absence and presence of Dirac electrons in silicene on substrates. Phys. Rev. B 87, 235435, doi:10.1103/PhysRevB.87.235435 (2013).

Wang, Y.-P. & Cheng, H.-P. Absence of a Dirac cone in silicene on Ag(111): First-principles density functional calculations with a modified effective band structure technique. Phys. Rev. B 87, 245430, doi:10.1103/PhysRevB.87.245430 (2013).

Tsoutsou, D., Xenogiannopoulou, E., Golas, E., Tsaias, P. & Dimoulas, A. Evidence for hybrid surface metallic band in (4 × 4) silicene on Ag(111). Appl. Phys. Lett. 103, 231604, doi:10.1063/1.4841335 (2013).

Moras, P., Mentes, T. O., Sheverdyaeva, P. M., Locatelli, A. & Carbone, C. Coexistence of multiple silicene phases in silicon grown on Ag(111). J. Phys.: Condens. Matter 26, 185001, doi:10.1088/0953-8984/26/18/185001 (2014).

Methods

DFT calculations. DFT calculations were performed with the Gaussian 09 software package42. We utilized a hybrid Becke-type three-parameter exchange functional43 paired with the gradient-corrected Lee, Yang, and Parr correlation functional (B3LYP) 44, 45 and the cc-pVTZ basis set 46–50 unless otherwise noted. The geometric parameters were fully optimized, and the minimized structures were confirmed to have no imaginary frequencies. To investigate the charge at each atom, natural population analysis (NPA)51–56 charges were calculated, as NPA charges are less basis-set dependent. Time-dependent density functional theory (TDDFT) calculations were carried out to obtain the HOMO-LUMO gap using the optimized ground state geometries 57. In all molecules studied here, the first excitation is mainly contributed by the HOMO-LUMO transition, although some of them are forbidden with zero oscillator strength. In Table 1, we list the first excitation energies as the HOMO-LUMO gap.

Figure 6. Two $D_{6h}$ structures. A: benzene-like, B: Si$_6$Li$_6$-like where metal moves between two silicon atoms.

Discussion

Here, we designed flat building blocks 1–5 to construct flat silicene using DFT calculations. We used substituents with $sp$-hybrid orbitals that act as electron donors. The minimum structure of all the obtained silicon polycyclic molecules 1–5 is flat. The charge is nearly neutral inside the ring and strongly negative at the ring edge due to the terminal BeH substituent. The HOMO and LUMO of 1–5 are $\pi$-orbitals. The designed molecules 1–5 could act as building blocks for flat silicene, which is a $\pi$-conjugated 2D sheet composed of six-membered silicon rings. The difference between the silicene constructed here and graphene is that BeH must be present at the terminal to stabilize the flat structure. In this sense, the molecules presented here are building blocks of silicene ribbons due to the existence of a terminal substituent. Flat six-membered silicon rings have long been desired in silicon chemistry and 2D silicon materials. In this study, flat hexasilabenzenes was realized, and it was confirmed that the extended ring molecules are also flat. The flatness of these building blocks opens the way to flat silicene ribbons or films constructed by them, but at present it does not guarantee the flatness of silicene ribbons or films. Further theoretical and experimental studies with careful design of the edge structure are required to realize flat silicene.

References

1. Guzmán-Verri, G. G. & Voon, L. C. L. Y. Electronic structure of silicon-based nanostructures. Phys. Rev. B 76, 075131, doi:10.1103/PhysRevB.76.075131 (2007).
2. Voon, L. C. L. Y., Zhu, J. & Schwingenschlögl, U. Silicene: Recent theoretical advances. Appl. Phys. Rev. 3, 040802, doi:10.1063/1.4944631 (2016).
3. Zhao, J. et al. Rise of silicene: A competitive 2D material. Prog. Mater. Sci. 83, 24–151, doi:10.1016/j.pmatsci.2016.04.001 (2016).
4. Tao, L. et al. Silicene field-effect transistors operating at room temperature. Nature Nanotech. 10, 227–231, doi:10.1038/NNANO.2014.325 (2015).
5. Peplow, M. Silicene makes its transistor debut. Nature 518, 17–18, doi:10.1038/518017a (2015).
6. Brumfiel, G. Sticky problem snarls wonder material. Nature 495, 152–153, doi:10.1038/495152a (2013).
7. Vogt, P. et al. Silicene: Compelling experimental evidence for graphene-like two-dimensional silicon. Phys. Rev. Lett. 108, 155501, doi:10.1103/PhysRevLett.108.155501 (2012).
8. Feng, B. et al. Evidence of silicene in honeycomb structures of silicon on Ag(111). Nano Lett. 12, 3507–3511, doi:10.1021/nl301047g (2012).
9. Gao, J. & Zhao, J. Initial geometries, interaction mechanism and high stability of silicene on Ag(111) surface. Sci. Rep. 2, 861, doi:10.1038/srep00861 (2012).
10. Kalitsas, D., Tsertseris, L. & Dimoulas, A. Structural evolution of single-layer films during deposition of silicon on silver: A first-principles study. J. Phys.: Condens. Matter 24, 442001, doi:10.1088/0953-8984/24/44/442001 (2012).
11. Guo, Z.-X., Furuya, S., Iwata, J.-I. & Oshiyama, A. Absence and presence of Dirac electrons in silicene on substrates. Phys. Rev. B 87, 235435, doi:10.1103/PhysRevB.87.235435 (2013).
12. Wang, Y.-P. & Cheng, H.-P. Absence of a Dirac cone in silicene on Ag(111): First-principles density functional calculations with a modified effective band structure technique. Phys. Rev. B 87, 245430, doi:10.1103/PhysRevB.87.245430 (2013).
13. Tsoutsou, D., Xenogiannopoulou, E., Golas, E., Tsaias, P. & Dimoulas, A. Evidence for hybrid surface metallic band in (4 × 4) silicene on Ag(111). Appl. Phys. Lett. 103, 231604, doi:10.1063/1.4841335 (2013).
14. Moras, P., Mentes, T. O., Sheverdyaeva, P. M., Locatelli, A. & Carbone, C. Coexistence of multiple silicene phases in silicon grown on Ag(111). J. Phys.: Condens. Matter 26, 185001, doi:10.1088/0953-8984/26/18/185001 (2014).
15. Feng, Y. et al. Direct evidence of interaction-induced Dirac cones in a monolayer silicone/Ag(111) system. Proc. Natl. Acad. Sci. USA 113, 14656–14661, doi:10.1073/pnas.1600341114 (2016).

16. Du, Y. et al. Quasi-free-standing epitaxial silicone on Ag(111) by oxygen intercalation. Sci. Adv. 2, e1600067, doi:10.1126/sciadv.1600067 (2016).

17. Heurleuse, A. et al. Experimental evidence for epitaxial silicone on diboride thin films. Phys. Rev. Lett. 108, 245501, doi:10.1103/PhysRevLett.108.245501 (2012).

18. Meng, L. et al. Buckled silicone formation on Ir(111). Nano Lett. 13, 685–690, doi:10.1021/nl304347w (2013).

19. Chiappe, D. et al. Two-dimensional Si nanosheets with local hexagonal structure on a MoS2 surface. Adv. Mater. 26, 2096–2101, doi:10.1002/adma.201304783 (2014).

20. Li, Z. et al. Observation of van HOVE singularities in twisted silicon multilayers. ACS Cent. Sci. 2, 517–521, doi:10.1021/acscentsci.6b00152 (2016).

21. Minkin, V. L., Glakhovtsev, M. N. & Simkin, B. Y. Aromaticity and antiaromaticity (Wiley & Sons, Inc., 1994).

22. Reed, A. E. & Weinhold, F. Natural localized molecular orbitals.

23. Reed, A. E. & Weinhold, F. Natural bond orbital analysis of near-Hartree–Fock water dimer.

24. Reed, A. E. & Weinhold, F. Natural hybrid orbitals.

25. Foster, J. P. & Weinhold, F. Natural bond orbital analysis of near-Hartree–Fock, water dimer. J. Chem. Phys. 78, 4066–4073, doi:10.1063/1.454134 (1983).

26. Reed, A. E., Weinstock, R. B. & Weinhold, F. Natural population analysis. J. Chem. Phys. 83, 735–746, doi:10.1063/1.449486 (1985).

27. Reed, A. E. & Weinhold, F. Natural localized molecular orbitals. J. Chem. Phys. 83, 1736–1740, doi:10.1063/1.449560 (1985).

28. Reed, A. E., Curtiss, L. A. & Weinhold, F. Internuclear interactions from a natural bond orbital, donor-acceptor viewpoint. Chem. Phys. Lett. 88, 899–926, doi:10.1016/s0009-2614(98)00084-5 (1984).

29. Carpenter, J. E. & Weinhold, F. Analysis of the geometry of the hydrosymethyl radical by the “different hybrids for different spins” natural bond orbital procedure. J. Mol. Struct. (THEOCHEM) 169, 41–62, doi:10.1016/0166-1280(88)80248-3 (1988).

30. Marques, M. A. L., Maia, N. T., Nogueira, F. M. S., Gross, E. K. U. & Rubio, A. Fundamentals of time-dependent density functional theory (Springer-Verlag, vol. 837, 2012).

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