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A molecule containing a stable carbon atom with all four bonds directed toward the same side of the nucleus

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ABSTRACT

The molecule $H@C_{20}H_{19}$ containing one stable carbon atom with all four single bonds directed toward the same side of the nucleus is reported here. Its geometry, electronic properties, vibrational frequencies and heat of formation have been calculated at the B3LYP/6-311+G(d,p) level of theory. The vibrational bands in the IR intensity of them have been discussed to be compared with future experimental identification. At the B3LYP/6-311+G(d,p) level, the heat of formation has been calculated using isodesmic reaction, 74.2 kcal mol^{-1}, larger than that of dodecahedrane, but smaller than that of the cubane C_8H_8. Thus we believe that $H@C_{20}H_{19}$ has sufficient stability to allow its experimental preparation.

1. Introduction

As carbon is tetravalent, it can form four single bonds spatially oriented toward the four corners of a tetrahedron, but in propellane [1] all four bonds at bridgehead carbons are directed toward the same side of the nucleus. Since each bridgehead carbon in propellane forms four bonds directed toward the same side of the nucleus, we designate this type of carbon ssC. In propellane, the central C–C bond between two ssCs is highly reactive [2] and tends to be broken, making it hard for the ssC structure to be maintained. Is there a molecule with a stable ssC? In order to answer this question, we studied an isomer of dodecahedrane with one encapsulated hydrogen atom in the cage, written as $H@C_{20}H_{19}$ in this work.

The two landmark syntheses of dodecahedrane, by Paquette [3] and by Prinzbach and Weber [4], were of great interest. It has been stated that "the dodecahedrane geometry is exquisite in its perfection" [4]. Owing to its unusual structure, dodecahedrane has also provided theorists with a severe test case for the calculation of geometry and properties. These include assessments of its vibrational frequencies [5], ordering of orbital energies [6,7], formation of inclusion compounds [7,8], NMR spin–spin coupling constants [9], and heat of formation [10].

Since all carbon and all hydrogen atoms in dodecahedrane are equivalent, $H@C_{20}H_{19}$ has a ssC and only one structure (see Fig. 1). To the best of our knowledge, a theoretical investigation of $H@C_{20}H_{19}$ has never been reported before. This paper is a theoretical attempt to study it by using DFT method at the B3LYP/6-311+G(d,p) level of theory [11,12]. Since the dodecahedrane and the molecule of interest have the same bonds: 30 carbon–carbon bonds and 20 carbon–hydrogen bonds. We use the following equation of the isodesmic reaction to calculate the heat of formation for the sake of understanding its thermodynamic stability.

$$C_{20}H_{20}\ (\text{dodecahedrane}) = H@C_{20}H_{19}$$

At 298 K and B3LYP/6-311+G(d,p) level of theory, its ΔH_f^0 is 74.2 kcal mol^{-1}, larger than that of dodecahedrane, but smaller than that of the cubane C_8H_8. Thus, we believe that $H@C_{20}H_{19}$ has sufficient stability to allow its experimental preparation.

2. Computational details

The full geometry optimization is performed by using the energy gradient method at the B3LYP/6-311+G(d,p) level of theory using Gaussian 03 program system [13]. After the optimization, the structure is nearly, but not quite of C_{3V} symmetry, and its symmetry converges to the C_1 point group. On the base of the optimized geometry, vibrational frequencies are also computed. Vibrational frequencies are determined firstly to verify the nature of the stationary point, secondly to use the sum of electronic energy and zero-point vibrational energy corrections for calculating the heat of formation, and thirdly to predict vibrational frequencies

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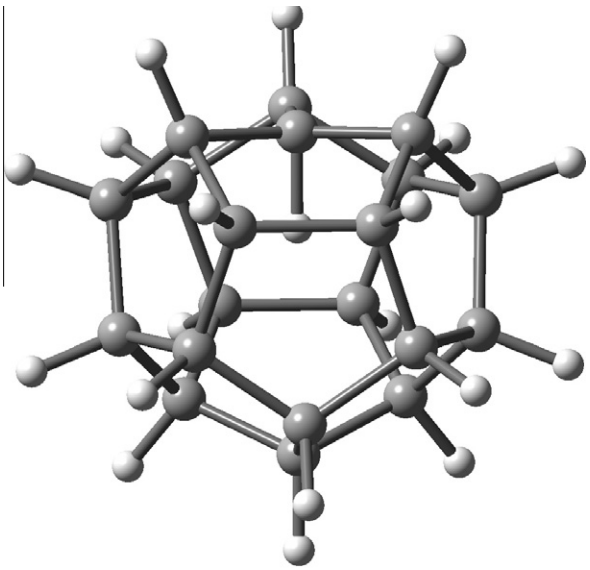

Fig. 1. The structure of H@$C_{20}H_{19}$.

of the unknown stable species for the sake of their future experimental identification by infrared (IR) spectroscopy. In order to understand the electronic and reactive properties, the net charges with natural bond orbital method and the probability density surfaces of HOMO-1 to LUMO+1 molecular orbitals have been discussed here.

3. Results and discussion

3.1. Geometry and electronic properties

The optimized structure is shown in Fig. 1. We use the two-dimensional schematic view (in Fig. 2) to show the distribution of pentagons and atoms in its cage, and the optimized bond lengths are also given in Fig. 2. Apart from ssC–H is 1.097 Å, other C–H bond lengths are at the range of 1.092–1.093 Å. The lengths of C–C bonds in pentagon which containing ssC are 1.486, 1.571, and 1.615 Å, others are at the range of 1.556–1.568 Å, which are close to those of dodecahedrane, 1.555 Å.

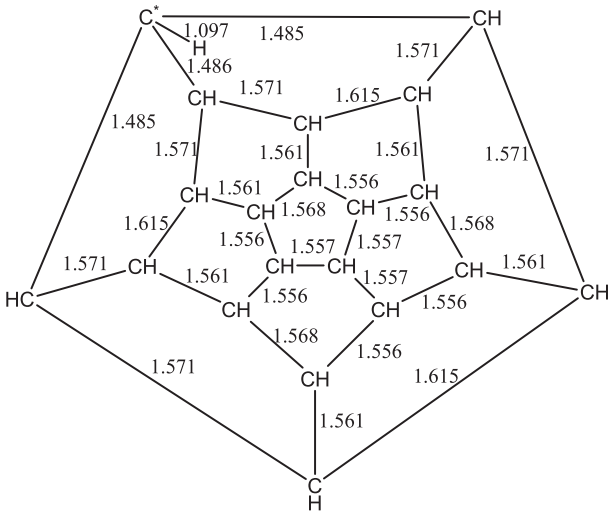

Fig. 2. The two-dimensional schematic view of H@$C_{20}H_{19}$ (the C* is ssC, the bond lengths in Å).

Table 1
Some computational properties of H@$C_{20}H_{19}$ and dodecahedrane $C_{20}H_{20}$.

Properties	H@$C_{20}H_{19}$	$C_{20}H_{20}$
E_{HOMO}/eV	−7.24 (*A*)[a]	−7.28 (G_g)
E_{LUMO}/eV	−0.26 (*A*)	−0.34 (A_g)
ΔE_{L-H}[b]/eV	6.98	6.94
E[c]/a.u.	−774.270250	−774.359519
Electronic state	^1A	^1A_g
Point group	C_1	I_h
Dipole moment/Debye	0.41	0.0
ZPE[d]/kcal mol^{-1}	223.8	224.0

[a] The orbital symmetry of HOMO and LUMO is given in parentheses.
[b] ΔE_{L-H} is the energy gap between HOMO and LUMO.
[c] *E* is the total energy of molecule computed at the same level by using Gaussian 03 program.
[d] ZPE is the zero-point vibrational energy determined at the same level, and the values were not scaled.

The ssC hybridizations in C–C and C–H bonds are $sp^{2.55}$ and $sp^{4.24}$, respectively. The hybridizations of other carbons in C–C and C–H bonds are in the range of $sp^{2.86}$–$sp^{3.06}$, and $sp^{3.20}$–$sp^{3.50}$, respectively.

Unfortunately, there is no single way in which to derive accurate electron populations at atoms, and different methods lead to different populations. Here we use the Weinhold's natural population analysis [14], which is based on the NBO procedure, to gain the net atomic charges of H@$C_{20}H_{19}$. It has been found that ssC has large negative net charges (q/e: −0.741) and are balanced by positive net charges on hydrogen atom bonding to ssC (q/e: 0.665). The net atomic charges of other carbon and hydrogen are in the range of −0.188 to −0.210*e* and 0.207 to 0.211*e*.

The energies of HOMO, LUMO and total molecule has been determined at the B3LYP/6-311+G(d,p) level of theory. All results are given in Table 1. Comparatively, those of dodecahedrane $C_{20}H_{20}$ are listed as well. Since the energies of HOMO for H@$C_{20}H_{19}$ and $C_{20}H_{20}$ are −7.24 and −7.28 eV, respectively, according to Koopman's theorem, the first ionization potential of $C_{20}H_{20}$ will be higher than that of H@$C_{20}H_{19}$. In fact, the energy of LUMO is sometimes considered as an approximation to the electron affinity. The LUMO energies for H@$C_{20}H_{19}$ and $C_{20}H_{20}$ are −0.26 and −0.34 eV, respectively. Their electron affinities are very close.

A large HOMO–LUMO gap has long been recognized as being correlated with kinetic and structural stability while a small gap is associated with reactivity [15–17]. The HOMO–LUMO gaps for H@$C_{20}H_{19}$ and $C_{20}H_{20}$ are 6.98 and 6.94 eV, respectively, the stability of H@$C_{20}H_{19}$ is similar to $C_{20}H_{20}$.

In order to gain insight into the properties of the HOMO-1 to LUMO+1, we plotted the probability density contours of the HOMO-1 to LUMO+1 at 0.02*e*/(a.u.)^3 isodensity surfaces in Fig. 3. As the contributions of all C–H bonds in HOMO are almost average, there is no active site to act as electron-donor partner in H@$C_{20}H_{19}$, but in LUMO the contributions are almost at the opposite side cage of the ssC, so the opposite side cage of the ssC in H@$C_{20}H_{19}$ is an active site to act as electron-acceptor partner. The evidence collected in Fig. 3 adds a novel contribution to the understanding of bonding feature in H@$C_{20}H_{19}$.

3.2. Vibrational frequencies

To verify the H@$C_{20}H_{19}$ is a real minimum on the potential energy hypersurface, its vibrational frequencies have been calculated. The predicted, unscaled vibrational frequencies are listed in Table 2. The smallest vibrational frequency for H@$C_{20}H_{19}$ is 372.0 cm^{-1}. The absence of imaginary vibrational frequency confirms that it corresponds to a true minimum on the potential energy hypersurface.