Rigorous Interpretation of Electronic Wave Functions. 3. Theoretical Confirmation of a Three-Center, Two-Electron C–H–C Bond in the *in*-Bicyclo[4.4.4]tetradecyl Cation

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Abstract: *Ab initio* quantum-mechanical calculations show that the D_3 structure of the *in*-bicyclo[4.4.4]tetradecyl (BCT) cation in which the bridging hydrogen is located at the midpoint between two carbon atoms corresponds to an energy minimum, therefore confirming the presence of a symmetrical three-center, two-electron C–H–C bond. This conclusion is further reinforced by the agreement between the calculated and the experimental IR and NMR spectra. Bonding in the BCT cation is rigorously represented by a set of 40 valence localized orbitals that fall into 8 distinct classes. The C–H–C bond is described by a single localized orbital, giving rise to the C–H covalent bond order of 0.504 and a negative charge of –0.228 on the bridging hydrogen.

Introduction

Although carbocations often have structures that defy common chemical wisdom, none of them is more unusual than that of the recently synthesized *in*-bicyclo[4.4.4]tetradecyl (BCT) cation.[1] The BCT cation, which is stable at room temperature and almost as weak as acetic acid, has only three peaks in both ^{1}H and ^{13}C NMR spectra, and therefore it appears to possess D_3 symmetry. On the basis of this and other evidence, the BCT cation has been assigned a nonclassical structure (Figure 1) with a bridging hydrogen bonded to two carbon atoms through an unusual three-center, two-electron C–H–C bond.[1]

The occurrence of such bonds is not as rare as one would imagine. In particular, ^{1}H NMR spectra of several species related to the cyclodecyl and bicyclo[3.3.1]nonyl cations reveal the presence of the C–H–C bonds.[2] Similar bonding has also been proposed in order to explain the mechanism of certain hydride-transfer rearrangements of carbocations.[3] The prototype H-bridged $C_2H_7^+$ cation was the subject of electronic structure calculations carried out as early as 1981[4] and then recently revisited.[5] Combined theoretical and experimental studies on the H-bridged $C_4H_9^+$ [6] and $C_8H_{15}^+$ [7] species have been reported and summarized in a review paper.[8] However, thanks to its high symmetry, the BCT cation is uniquely suited for electronic structure calculations capable of providing the ultimate theoretical proof for the presence of the C–H–C bond. Results of such calculations are reported in this paper.

Computational Techniques

The geometry of the *in*-bicyclo[4.4.4]tetradecyl (BCT) cation was optimized at both the HF/6-31G** and MP2/6-31G** levels of theory. D_3 symmetry was maintained throughout the calculations, which were carried out with the GAUSSIAN 90[9] suite of programs. The HF/6-31G** wave function was analyzed with the topological theory of atoms in molecules.[10] The VECAIM program[11] was employed in the calculation of atomic properties. The bridging hydrogen and the carbon atoms linked to it were found to be refractory to the usual algorithm for the determination of atomic boundaries and therefore the PROMEGA program[12] was used in calculations of their properties. The resulting atomic overlap matrices (AOMs) were used to compute the AOM-localized orbitals[13] and the covalent bond orders.[14]

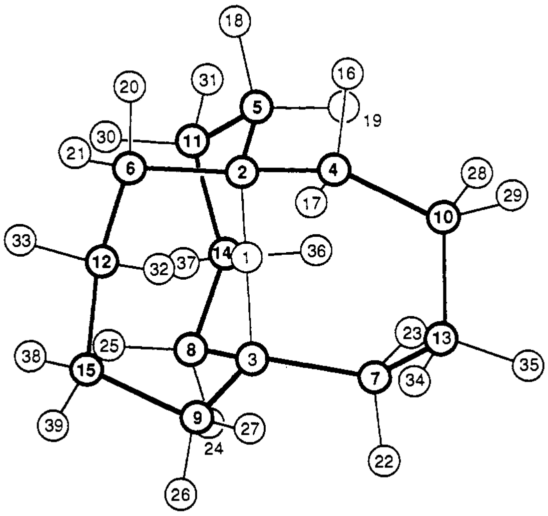

Figure 1. Molecular skeleton of the *in*-bicyclo[4.4.4]tetradecyl cation. The thick lines denote the C–C framework and the thin ones stand for the C–H bonds.

The ^{1}H and ^{13}C NMR shifts were calculated at the HF/6-311G** level of theory for both the HF/6-31G** and MP2/6-31G** optimized geometries. In order to compute the NMR shifts, the recently developed efficient GIAO-CPHF program of Pulay and Wolinski[15] was interfaced

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Table I. The Optimized Bond Lengths, Bond Angles, and Torsional Angles[a]

		Bond Lengths (Å)			
C_2–H_1	1.231 (1.249)	C_3–C_4	1.514 (1.522)	C_4–C_{10}	1.533 (1.535)
C_4–H_{16}	1.097 (1.089)	C_4–H_{17}	1.091 (1.083)	C_{10}–H_{28}	1.092 (1.086)
C_{10}–H_{29}	1.091 (1.084)				
		Bond Angles (deg)			
C_4–C_2–H_1	102.0 (102.3)	C_4–C_{10}–H_{28}	110.8 (110.9)		
C_2–H_4–H_{17}	109.9 (109.7)	C_2–C_4–H_{16}	104.7 (105.1)		
C_{10}–C_4–C_2	116.3 (116.6)	C_4–C_{10}–H_{29}	107.0 (106.8)		
		Torsional Angles (deg)			
C_7–C_3–H_1–C_4	–37.9 (–34.6)	C_{10}–C_4–C_2–H_1	45.7 (43.2)		
H_1–C_2–C_4–H_{16}	166.9 (164.5)	H_1–C_2–C_4–H_{17}	–79.0 (–81.5)		
C_2–C_4–C_{10}–H_{28}	57.4 (58.7)	C_2–C_4–C_{10}–H_{29}	–187.4 (–186.4)		

[a] MP2/6-31G** values followed by HF/6-31G** values in parentheses; see Figure 1 for atom numbering.

with the TURBOMOLE system[16] and its disk-based CPHF procedure was replaced by a direct algorithm.[17] The calculated averaged shieldings were converted to the δ values (relative to TMS) by noting that the HF/6-311G** values of the ^{1}H and ^{13}C shieldings in methane are 31.88 and 197.09 ppm,[15] respectively, and the corresponding chemical shifts equal 0.0 and –2.3 ppm.[18]

Electronic Structure of the *in*-Bicyclo[4.4.4]tetradecyl Cation

As revealed by calculations of vibrational frequencies, at the HF/6-31G** level of theory the D_3 structure of the BCT cation corresponds to a minimum on the potential energy hypersurface. The optimized geometrical parameters are listed in Table I. The entire cation cage is highly twisted as reflected by the torsional angle C_7–C_3–H_1–C_4 of ca. 35°. Although the bridgehead angle C_4–C_2–H_1 of ca. 102° is rather small for a tetrahedral carbon atom, the C–C bonds have the usual lengths of ca. 1.5 Å. The same is true about the 24 external C–H bonds with the lengths of ca. 1.1 Å.

As dictated by the overall molecular symmetry of the BCT cation, the bridging hydrogen has to be collinear with its neighboring carbon atoms and be positioned at the midpoint between them. Such a geometrical arrangement gives rise to two identical C–H distances, which are found to be unusually large for a normal C–H bond. At the HF/6-31G** level of theory, the bridging C–H distance is equal to 1.249 Å and decreases to 1.231 Å upon inclusion of electron correlation. This means that, in contrast to the common trend, the Hartree–Fock approximation seems to *underestimate* the strength of the C–H–C bond. It should also be mentioned that the calculated bridging C–H distances are in reasonable agreement with the previously published[1] AM1 and HF/3-21G values.

The unusual geometry of the BCT cation can be easily rationalized when the computed electronic wave functions are analyzed with the help of rigorous interpretive tools.[19] Such an analysis involves theoretical approaches, including the topological theory of atoms in molecules[10] and its extensions,[13,14] that do not explicitly refer to basis functions as "atomic orbitals" and therefore are capable of providing unbiased descriptions of the electronic structures of diverse chemical systems.

The atomic charges and covalent bond orders obtained from the HF/6-31G** wave function are compiled in Table II. The positive electric charge of the cation is completely delocalized outside of the central C–H–C moiety, with the bridging hydrogen actually bearing a slightly negative charge. In agreement with the normal bond lengths, the covalent bond orders are close to 1.0, except for the bridging C–H bonds that possess bond orders of only 0.504.

Table II. The HF/6-31G** Atomic Charges and Covalent Bond Orders[a]

atom	charge	bond	covalent bond order
H_1	–0.228	C_2–H_1	0.504
C_2	–0.021	C_2–C_4	0.991
C_4	0.189	C_4–C_{10}	0.988
C_{10}	0.198	C_{10}–C_{13}	0.997
H_{16}	–0.023	C_4–H_{16}	0.945
H_{17}	–0.046	C_4–H_{17}	0.954
H_{28}	–0.071	C_{10}–H_{28}	0.961
H_{29}	–0.036	C_{10}–H_{29}	0.961

[a] See Figure 1 for atom numbering.

Table III. The Valence HF/6-31G** Localized Orbitals[a]

orbital[b]	description
15 (16,17,18,19,20)	16.1% ionic C_2–C_4 bond, 94.6% localized
21 (22,23)	purely covalent C_{10}–C_{13} bond, 94.4% localized
24 (25,26,27,28,29)	7.1% ionic C_4–C_{10} bond, 94.1% localized
30 (31,32,33,34,35)	1.7% ionic C_4–H_{17} bond, 95.3% localized
36 (37,38,39,40,41)	1.6% ionic C_{10}–H_{29} bond, 95.7% localized
42 (43,44,45,46,47)	0.8% ionic C_4–H_{16} bond, 94.8% localized
48 (49,50,51,52,53)	3.9% ionic C_{10}–H_{28} bond, 95.5% localized
54	C_2–H_1–C_3 tricentric bond, localized 53.1% on the hydrogen and 20.6% on each of the carbons

[a] See Figure 1 for atom numbering. [b] Localized orbitals ordered according to increasing negative kinetic energies with orbitals related by symmetry listed in parentheses.

The bonding in the BCT cation is remarkably simple. Within the Hartree–Fock approximation, there are 56 occupied localized orbitals (LMOs), 14 of which describe core electrons. The 40 valence localized orbitals fall into 8 distinct categories (Table III). LMOs 15–53, which are highly localized, describe bicentric bonds with varying degrees of ionicity. In particular, the ionicities of the C–C bonds decrease with the increasing distance from the C–H–C moiety. The last, single localized orbital (LMO 54, Table III) provides explicit evidence for the presence of a three-center, two-electron C–H–C bond in the BCT cation.

Spectroscopic Properties of the *in*-Bicyclo[4.4.4]tetradecyl Cation

As mentioned above, an energy minimum is attained when the bridging hydrogen is located at the midpoint between the neighboring carbon atoms. At the HF/6-31G** level of theory, one finds a vibrational mode at 2019 cm^{-1}, which corresponds mainly (the normal mode coefficient equal to 0.93) to displacement of the bridging hydrogen along the D_3 symmetry axis. Because of the substantial charge on the bridging hydrogen atom, the corresponding IR absorption is predicted to be very strong, with the oscillator strength ca. 3 orders of magnitude higher than that of the usual C–H stretching vibration. The vibrational mode, which is predicted to be Raman inactive, obviously corresponds to the experimentally observed[1] strong IR absorption at 2113 cm^{-1}. One should note that, since the strength of the C–H–C bond is *underestimated* at the Hartree–Fock level, one may expect improved agreement between the theoretical and experimental vibrational frequencies upon inclusion of electron correlation.

Ab initio calculations of NMR shifts (often carried out with the somewhat less accurate[20] IGLO[21] approach) have repeatedly

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Table IV. The HF/6-311G** ^{13}C and ^{1}H NMR Chemical Shifts[a]

atom	chemical shift relative to TMS (ppm)		
	at HF/6-31G** geometry	at MP2/6-31G** geometry	exptl[b]
H_1	−9.66	−10.06	−3.46
C_2	136.2	132.1	139.3
C_4	35.4	35.1	41.6
C_{10}	18.1	19.1	19.3
H_{16}	1.09	1.25	2.5
H_{17}	1.93	2.19	2.5
H_{28}	1.01	1.23	1.9
H_{29}	1.27	1.48	1.9

[a] See Figure 1 for atom numbering. [b] Reference 1.

proven very successful in elucidating structures of carbocations.[22] The ^{13}C chemical shifts of the positively charged carbon atoms in typical carbocations range from 250 to 350 ppm,[18] but the experimental values[1] for the carbons in the BCT cation are much smaller. This phenomenon, which is undoubtedly associated with the pronounced charge delocalization, is accurately reproduced by the HF/6-311G** shifts calculated at both the HF/6-31G** and MP2/6-31G** geometries within the GIAO-CPHF approach (Table IV).

The experimentally observed ^{1}H NMR spectrum of the BCT cation[1] consists of three broad absorptions at 2.5, 1.9, and −3.46 ppm. The first two absorptions can be assigned to the H_{16}–H_{27} and H_{28}–H_{39} protons (Figure 1), respectively, for which the chemical shifts ranging from 1.23 to 2.19 ppm are calculated (Table IV). The large upfield shift of the bridging proton is also reproduced by our calculations, but the quantitative agreement is not satisfactory. The large difference of ca. 6.5 ppm between the theoretical and experimental shifts is puzzling, taking into account the fact that the HF/6-311G** GIAO-CPHF ^{1}H shifts are usually accurate within 1–2 ppm. In principle, the discrepancy could be attributed to an insufficient basis set, the neglect of electron correlation effects, or inaccurate geometry. However, the last possibility does not appear to be the probable cause, as replacing the HF/6-31G** optimized geometry by the MP2/6-31G** one does not bring about any improvement. Another possible explanation is that the bridging hydrogen undergoes relatively large vibrational motions, and therefore the observed vibrationally averaged shift cannot be directly compared with the frozen-nuclei theoretical value.

Conclusions

Ab initio electronic structure calculations show that the D_3 geometry of the *in*-bicyclo[4.4.4]tetradecyl (BCT) cation with the bridging hydrogen located at the midpoint between two carbon atoms corresponds to a minimum on the potential energy hypersurface. Therefore, the presence of a symmetrical three-center, two-electron bond between two carbon atoms and a collinear hydrogen is confirmed in this unusual cation. The electronic structure of the BCT cation is rigorously described in terms of 40 valence localized orbitals that fall into 8 distinct classes. Seven of these classes correspond to ordinary C–H and C–C bicentric orbitals, resulting in covalent bond orders close to 1.0 for the corresponding bonds. The C–H–C bond is described by a single localized orbital, giving rise to the C–H covalent bond order of 0.504 and a negative charge of −0.228 on the bridging hydrogen.

That the experimentally observed BCT cation indeed has D_3 structure is further reinforced by the agreement between the calculated and the experimental IR and NMR spectra. However, quite disappointingly, the calculated chemical shift of the bridging hydrogen differs substantially from its experimental counterpart. At present, no satisfactory explanation for this discrepancy is available.

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