Characteristic Frequencies of Hydrogen-bridged Carbocations. IR Spectra and *Ab Initio* Calculations of the Nonclassical Structures of the Cyclooctyl Cation

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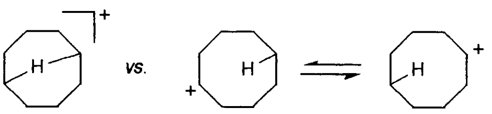
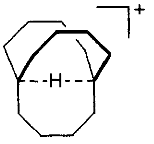
The symmetrically H-bridged structure of the cyclooctyl cation is confirmed definitively by the characteristic IR vibration at 1845 cm^{-1} and by the agreement of the IGLO chemical shifts calculated with MP2/6-31G* geometry of the chair–boat (C_s) conformation with the experimental NMR values.

Transannular μ-hydrido bridging is reasonably well established in some mono- and bi-cyclic carbocations.[1–3] The upfield NMR chemical shifts of the bridging hydrogens are characteristic. However, previous investigations have not always been able to differentiate between static symmetrically bridged or rapidly equilibrating unsymmetrical (classical) structural alternatives (Scheme 1). The NMR time scale is too slow to distinguish between these two possibilities, although isotopic perturbation has been employed in some cases.[3]

We have now applied IR spectroscopy[4] and IGLO chemical shift calculations[5] to this problem and have chosen the cyclooctyl cation for study. Our expectations were based on



Scheme 1



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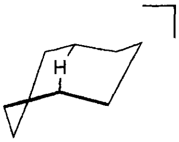
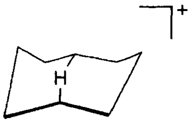


2a



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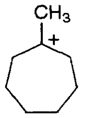

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Table 1 Selected optimized parameters (*d*/Å and ∠/°)

	HF/6-31G*	MP2/6-31G*	AM1
C_s			
$d(C^1C^2)$	2.338	2.328	2.423
$d(C^1C^3)$	1.510	1.499	1.497
$d(C^1C^5)$	1.517	1.505	1.497
$d(C^3C^7)$	1.535	1.533	1.519
$d(C^5C^8)$	1.535	1.534	1.520
$d(H^bC^1)$	1.278	1.270	1.339
$d(C^1H^1)$	1.082	1.098	1.118
$\angle(C^1H^1C^2)$	132.47	132.89	129.6
$\angle(H^bC^1H^1)$	92.97	92.21	95.96
C_{2v}			
$d(C^1C^2)$	2.331	2.320	2.414
$d(C^1C^3)$	1.517	1.505	1.497
$d(C^3C^7)$	1.538	1.539	1.522
$d(H^bC^1)$	1.267	1.261	1.336
$d(C^1H^1)$	1.083	1.099	1.119
$\angle(C^1H^bC^2)$	133.91	133.96	129.16
$\angle(H^bC^1H^1)$	92.16	91.07	95.06

the IR spectrum reported for a symmetrically H-bridged carbocation, McMurry's very stable *in*-bicyclo[4.4.4]-1-tetradecyl cation **1**.[2b] This exhibits a characteristic C–H–C (⟷) vibration at 2113 cm^{-1}. The cyclooctyl cation **2** is not easy to observe, since the half life for rearrangement to the methylcycloheptyl cation **3** is only 17 min at −142 °C.[1a] Nevertheless the IR spectrum of **2** was obtained by using the modified method of Vančik and Sunko.[4] SbF$_5$ (290 mg) and cyclooctyl chloride (20 mg) were codeposited on a NaCl disc at −165 °C. Even at this low temperature, a broad signal at 1845 cm^{-1} developed (Fig. 1) akin to that of **1**.[3b] After 15 min at −165 °C, the intensity of this characteristic signal did not change, but it diminished at higher temperature and vanished completely at −110 °C. Rearrangement to the methylcycloheptyl cation **3** had taken place.[1a]

Geometries for the C_s (chair–boat) **2a** and C_{2v} (chair–chair) **2b** were optimized by *ab initio* methods at HF/6-31G* and MP2/6-31G*.[6,7] At the last level, **2a** is 16.5 kJ mol^{-1} lower in energy than **2b**, in agreement with the experimental conclusions.[1a] The NPA (natural population analysis)[8] hybridisation ratio of the C^1 bond involving H^b, sp^{12}, corresponds to almost pure p-orbital participation. Selected geometry parameters

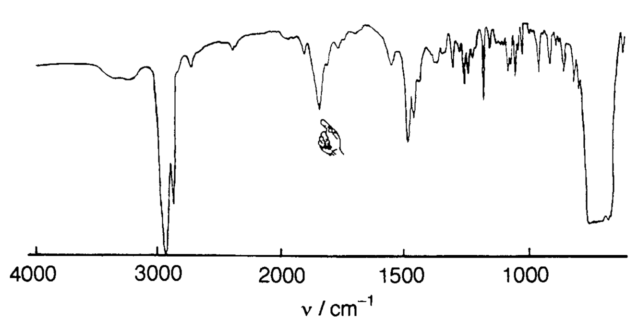

Fig. 1 IR spectrum of the cyclooctyl cation at −165 °C in an SbF$_5$ matrix

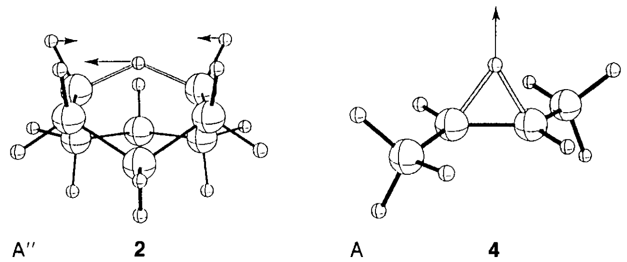

Fig. 2 Normal modes of the characteristic CHC vibrations of the cyclooctyl (1845 cm^{-1}) and the 2-butyl (2175 cm^{-1}) cations

Table 2 IGLO chemical shift calculations for the cyclooctyl cation at various theoretical levels

		$\delta(^{13}C)$					$\delta(^1H)$	
Symmetry	IGLO[a] basis // geometry	C^1	C^3	C^5	C^7	C^8	H^b	H^1
C_{2v}	DZ[a] // HF/3-21G	153.4	27.9		45.0		−16.6	8.6
	DZ // HF/6-31G*	147.8	26.2		41.4		−15.2	8.3
	Bas221[b] // HF/6-31G*	156.3	36.4		50.6		−10.8	7.9
	Bas221[b] // MP2/6-31G*	152.5	37.2		52.6		−10.4	8.0
C_s	DZ // AM1	158.7	27.9	27.0	32.2	42.9	−12.0	9.3
	DZ // HF/3-21G	148.3	24.4	23.6	29.9	39.7	−15.9	8.3
	DZ // HF/6-31G*	144.2	23.4	22.2	28.7	36.7	−14.7	8.1
	Bas221[b] // HF/6.31G*	153.1	32.9	32.4	37.2	46.1	−10.7	7.7
	Bas221[b] // MP2/6-31G*	149.4	33.4	33.6	38.8	47.4	−10.5	7.8
	expt (*vs.* SiMe$_4$)[1a]	151.7	31.5	31.5	41.3	50.6	−7.7	7.9

[a] IGLO = individual gauge for localized orbitals; DZ = double zeta. [b] Bas221: IGLO basis II used for C and the bridging H; DZ for the remaining Hs.

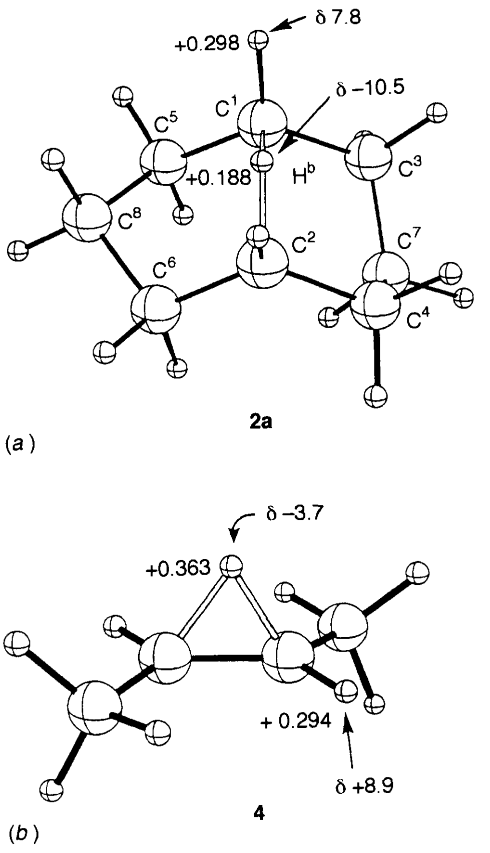

Fig. 3 NPA H charges and IGLO δ(^{1}H) chemical shifts of (*a*) the cyclooctyl **2** and (*b*) the 2-butyl cation **4**. Note the lack of correspondence. The bridging hydrogens are positively (not negatively) charged to different degrees, higher in **4** and lower in **2**.

Table 3 NPA and Mulliken charges (atomic units) calculated at MP2/6-31G* using the Hartree–Fock wave function

	Cyclooctyl cation			2-Butyl cation	
	NPA ρ	Mulliken ρ		NPA ρ	Mulliken ρ
C^1	−0.079	−0.229		−0.107	−0.090
C^3	−0.483	−0.353		−0.705	−0.393
C^5	−0.486	−0.353			
C^7	−0.436	−0.351			
C^8	−0.419	−0.355			
H^b	0.188	0.179		0.363	0.218
H^1	0.298	0.300		0.294	0.265
H$^{2-9}$	0.234–0.284	0.201–0.251	H$^{2-4}$	0.262–0.294	0.186–0.265

are compared in Table 1 along with those obtained from AM1[9] semi-empirical theory (using the NLLSQ gradient minimizer).

Because of technical limitations harmonic frequencies could only be computed at HF/6-31G*. After scaling by 0.89[6] the frequencies of the high intensity bridging hydrogens are 1825 cm^{-1} (1210 km mol^{-1}) (C_{2v}) and 1776 cm^{-1} (1188 km mol^{-1}) (C_s).† Both agree reasonably well with the experimental 1845 cm^{-1} value. In contrast, the characteristic signal of the H-bridged 2-butyl cation **4** at 2175 cm^{-1} (exp.; calc. 2125 cm^{-1}, MP2/6-31G**, scaled by 0.94)[4b] has a significantly lower calculated intensity (23.4 km mol^{-1}) and corresponds to a different vibrational mode. The vectors are compared in Fig. 2. Note for **2** the parallel (⟷) and for **4** a perpendicular (↕) movement of the bridging H with respect to the bridged C–C bond **2** and **4**, respectively. The intensities are larger in **2** as the μ-hydrogen moves from one carbon to another.

The four ^{13}C NMR signals observed experimentally[1a] point to a chair–boat conformation **2a**. This C_s and also C_{2v} structures were employed for IGLO chemical shift calculations on various *ab initio* geometries (Table 2). A high quality IGLO basis set is required to describe such systems. The ^{13}C and ^{1}H chemical shifts calculated at HF/6-31G* and MP2/6-31G* geometries for the C_s structure are in quite good agreement with the experimental values. The δ(^{1}H) values for the highly shielded (H^b) and deshielded (H^1) hydrogens (Fig. 3*a*) are reproduced reasonably well. Supported by semi-empirical calculations[1b] on model systems, it was postulated that the electron density on these hydrogens, higher for H^b and lower for H^1, are responsible for these chemical shifts. The natural charges (natural population analysis)[8] as well as the Mulliken charges derived from the *ab initio* wavefunctions do not provide convincing support for this interpretation (Table 3). Moreover the charge (+0.363) on H^b in the 2-butyl cation is even larger than of H^2, +0.294, whereas the IGLO/DZ chemical shifts predict the opposite degree of shielding (Fig. 3*b*) No charge–chemical shift correlation is generally to be expected;[10] the origin of NMR chemical shifts is far more complex.[11]

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† In our experience, calculations at electron correlation (MP2) level generally give higher frequencies, but such computation is not feasible at present.

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