Confirmation of the H-Bridged Structure of the 2-Butyl Cation by Comparison of Experimental and *Ab Initio* IR Frequencies

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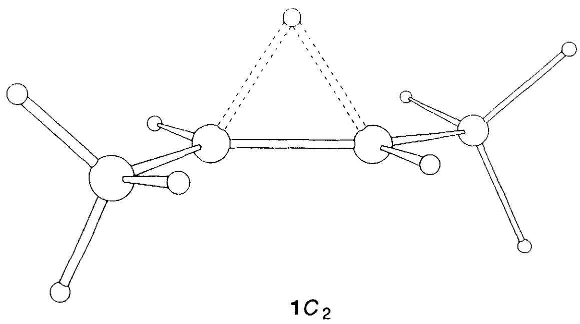
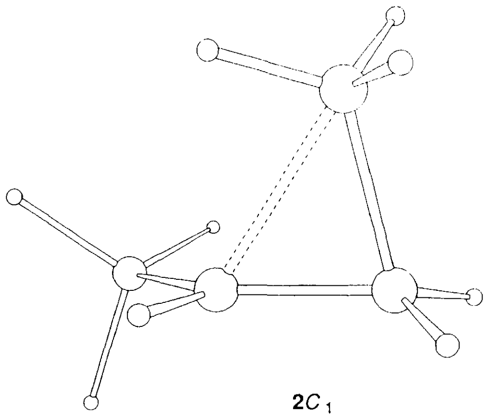
The IR spectrum of the 2-butyl cation, measured at −125 °C in an SbF_5 matrix and calculated *ab initio* (MP2(FULL)/6-31G*), is characterized by a C(H ↕) C peak at 2175 cm^{-1} assigned to the nonclassical H-bridged (C_2-symmetry) structure **1**.

Even though the 2-butyl cation can be observed directly in super acid media, it has been difficult to establish the preferred structure with certainty.[1–4] The potential energy surface is quite flat, as the degenerate rearrangements which interconvert the three inner Hs [as well as C(2)–C(3) and C(1)–C(4)] could not be slowed on the NMR time scale at −140 °C[2a] nor even by CPMAS measurements at −190 °C.[2b] The temperature dependence of both the deuterium and the ^{13}C isotope effects, observed by Saunders and Walker in the NMR,[2c] could best be fit by assuming that two isomers were present, the more stable having an H-bridged structure (*e.g.* the *trans* form, **1**). In contrast, recent ESCA experiments (albeit under solid-state conditions where the purity or nature of the species being observed was not established independently by other methods and the nature of the substance measured on the surface may differ from that in the bulk) were interpreted in terms of a partially methyl-bridged structure, *e.g.* **2**.[3]

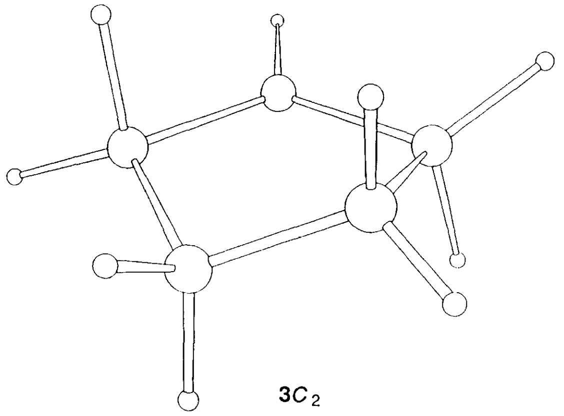
Our extensive recent computational search of the $C_4H_9^+$ potential energy surface at high *ab initio* levels found both **2** (C_1-point group) and **1** (C_2-symmetry) to be 2-butyl cation minima.[4] At MP4sdtq/6-31G**//MP2(FULL)/6-31G**[5] [corrected by the zero-point energies newly calculated at the MP2(FULL)/6-31G* level], **1** is only 1.9 kJ mol^{-1} more stable than **2**. When entropy is taken into account, the free energy difference (at 150 K, 10^4 Pa) is 1.2 kJ mol^{-1}. Although



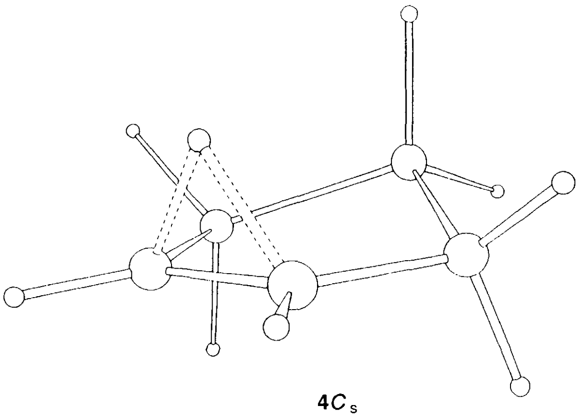
1C_2



2C_1



3C_2



4C_s

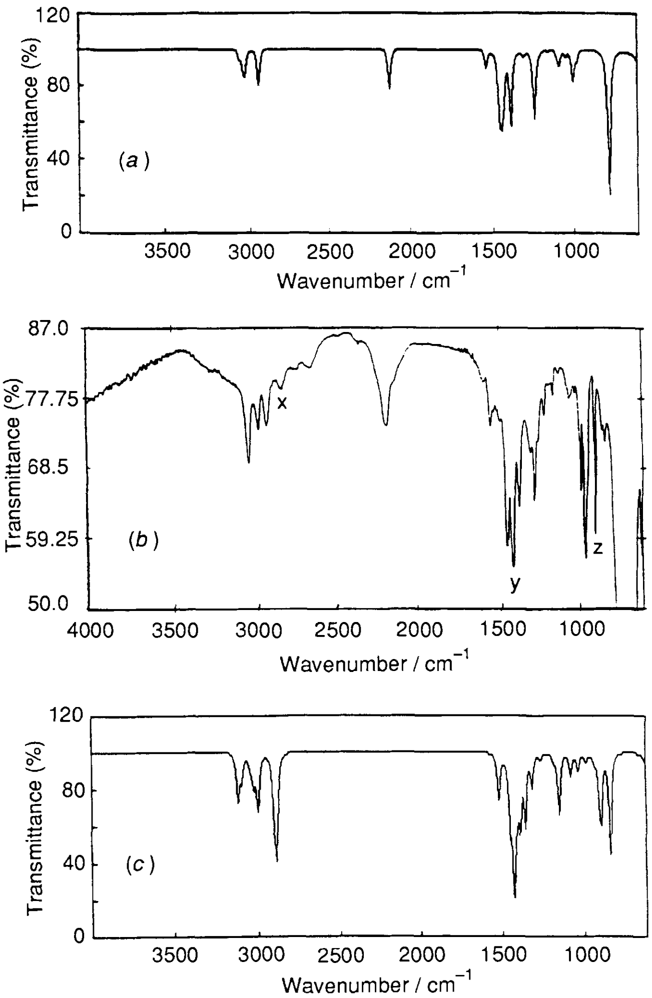


Fig. 1 Comparison of the simulated IR-spectra of calculated forms **1** (*a*) and **2** (*c*) (MP2/6-31 G*), with (*b*) the measured spectrum of the 2-butyl cation at −125 °C. The peak 'x' is due to the *tert*-butyl cation 'y' arises from SbF_5, and 'z' from $Sb_2F_{10}Cl^-$.[9d]

referring to the isolated state, this small energy difference (which agrees with the *ca* 1.7 kJ mol^{-1} deduced by Saunders)[2c] implies that the two species might be in equilibrium.

IGLO chemical shift calculations[6] are generally very useful for deciding between carbocation structures with similar energies.[7,8] The IGLO predictions for various geometries are compared with experimental NMR data. The cyclopentyl cation affords a pertinent example.[8] Even though also calculated to be only 1.3 kJ mol^{-1} less stable than the hyperconjugatively stabilized global minimum **3** (C_2), the symmetrically H-bridged form **4** (C_s) could be ruled out. The IGLO chemical shifts for **3** agreed with experiment, but not those computed for **4**. While the correspondence of the IGLO $\delta^{13}C$ data for **1** with experiment was better than the values calculated for **2**,[4] the error [10–15 ppm for C(2)–C(3)] was somewhat larger than found for other carbocations.[7,8]

We have now applied another spectroscopic method to the 2-butyl cation structure problem: the comparison of experimental[9] with theoretical (*ab initio*)[5] vibrational spectra. This is the first IR investigation of a carbocation expected to have a 1,2-H-bridged structure which includes the particularly significant but usually sparsely populated 2000 cm^{-1} region. (Only a partial spectrum, *i.e.* above *ca.* 3000 cm^{-1}, of the bridged vinyl cation in the gas phase has been reported.)[10] As the data collected in Table 1 demonstrate, frequencies near 2150 cm^{-1} [due to the symmetrical stretching vibration C(H$\updownarrow$)C, perpendicular to the C–C axis] are predicted computationally to be quite characteristic of three-centre C(H)C bonding when a formal C–C single bond is present. (As the H-bridged vinyl cation has a formal C=C double bond,

Table 1 Characteristic 'perpendicular stretching' [C(H $\updownarrow$) C] frequencies of symmetrically 1,2-H bridged carbocations

1,2-H Bridged carbocation	Point group	C(H $\updownarrow$) C Frequencies, cm^{-1} computed (level)[a]	NIMAG[b,c]	Expt. freq.
HC(H)CH+ (Vinyl) (1,2-Ethenyl)	C_{2v}	2317 (MP2(FU)/6-31G**)	(0)	*cf.* ref. 14
		2306 (MP2(FU)/6-31G*)	(0)	
		2229 (HF/6-31G**)	(0)	
		2261 (HF/6-31G*)	(0)	
$H_2C(H)CH_2$+ (1,2-Ethyl)	C_{2v}	2137 (MP2(FU)/6-31G**)	(0)	
		2126 (MP2(FU)/6-31G*)	(0)	
		2029 (HF/6-31G**)	(0)	
		2048 (HF/6-31G*)	(0)	
2,3-Butyl **1**	C_2	2107 (MP2(FU)/6-31G*)	(0)	2175s[d]
		2036 (HF/6-31G*)	(1)[c]	
1,2-Cyclobutyl	C_s	2126 (MP2(FU)/6-31G**)	(0)	
		2024 (HF/6-31G*)	(1)[c]	
1,2-Cyclopentyl **4**	C_s	2014 (HF/6-31G*)	(1)[e]	absent[f]
Edge-protonated benzene (1,2-C_6H_7+)	C_s	1980 (HF/6-31G*)	(1)[e]	
2,3-*exo*-Norbornyl	C_s	1998 (HF/6-31G*)	(1)	
2,3-*exo*-Norbornenyl	C_s	1981 (HF/6-31G*)	(1)	
2,3-*endo*-Norbornenyl	C_s	2032 (HF/6-31G*)	(1)	
$(CH_3)_2C(H)C(CH_3)_2$+ (2,3-Dimethyl-2,3-butyl)	C_2	2007 (HF/6-31G*)	(1)	

[a] See ref. 5 for a general description and details of the computation levels. The MP2 frequencies were calculated analytically with the CADPAC program (ref. 11) and were scaled by 0.94 (by 0.89 at HF, see refs. 5 and 12). [b] Minima have zero imaginary frequencies (NIMAG = 0). [c] Transition structures have NIMAG = 1, but some of these (as noted) are artifacts at HF levels. This may be the case for other HF results as well. [d] This work. [e] See ref. 8. Frequencies at MP2 levels not available due to current computational limitations. [f] Ref. 9(*g*).

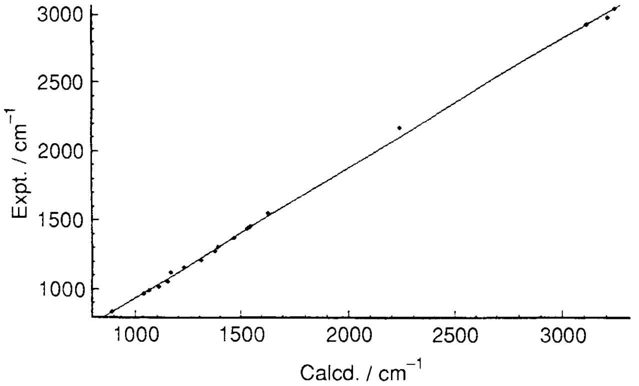


Fig. 2 Correlation between the experimental and the calculated (MP2/6-31G*) frequencies of 2-butyl cation (C_2-form); m = 0.945, cc = 0.9995

the corresponding frequency is predicted to be somewhat higher.)†

Experimentally, B(H $\updownarrow$)B frequencies in the 1800–2050 cm^{-1} range are assigned to the similar three-centre bonds in numerous hydrogen-bridged electron deficient boron compounds.[13] The absence of a *ca.* 2150 cm^{-1} band in the IR spectrum of the cyclopentyl cation[9e] provides more evidence against the symmetrically H-bridged structure **4** for this species.[8]

The predicted IR spectra (calculated[14,15] at MP2/6-31G*) for the 2-butyl cation isomers, **1** [Fig. 1(*a*)] and **2** [Fig. 1(*c*)], show many clear-cut differences. Note, in particular, the presence of the *ca.* 2100 cm^{-1} absorption (Table 1) in Fig. 1(*a*),[16] and its absence in Fig. 1(*c*).[16]

Table 2 Calculated [MP2 (FU)/6-31G*] (**1**, **2**) (scaled by 0.94) and experimental frequencies and intensities

2 (scld.) cm^{-1}	**2** Int. /km mol^{-1}	**1** (scld.) cm^{-1}	**1** Int. /km mol^{-1}	Expt. /cm^{-1}	Expt. int.[a]
3121	16.9	3047	0.3	3053	s
3098	9.0	3047	4.7		
3050	3.3	3024	8.9		
3038	2.7	3015	4.5	2988	m
3026	9.2	3012	2.9		
3003	12.9	3011	4.0		
2997	7.7	2928	18.3	2937	m
2905	18.8	2928	2.7		
2889	33.8	2107	23.4	2175	s
1525	16.8	1535	10.4	1552	m
1457	21.4	1455	31.2	1454	vs
1434	43.9	1442	27.3	1444	vs
1420	10.1	1428	15.1		
1409	4.6	1426	7.8		
1396	21.1	1383	7.0		
1365	23.3	1382	37.3	1375	vs
1321	10.8	1307	2.7	1306	s
1269	2.2	1293	1.5	1281	s
1188	2.4	1234	40.3	1213	m
1157	21.9	1151	1.3	1157	m
1086	8.7	1094	2.8	1122	w
1038	6.7	1083	8.3	1059	m
989	3.3	1044	4.0	1022	w
931	3.0	999	18.4	991	s
901	15.9	975	5.2	964	vs
889	17.8	837	0.3	899	vs
832	37.9	776	83.2	835	s
567	56.8	531	344.5		
427	19.4	474	0.0		
367	12.6	265	3.6		
254	37.4	248	0.0		
209	0.8	221	13.0		
143	1.9	183	0.8		

[a] w: weak, m: medium, s: strong, vs: very strong.

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† McMurray *et al.* have observed an IR frequency of 2113 cm^{-1} for the (CC unsupported) transannular H-bridged cage cation, bicyclo-[4.4.4]tetradecan-1-yl.[11] However, this refers to a different vibration (unsymmetrical CHC stretching); such frequencies can be expected to vary to a greater extent from system to system. [Details of our observation of an 1840vs cm^{-1} absorption for the transannularly H-bridged cyclooctyl cation (*cf.* ref. 12), as well as a general discussion of the spectroscopic features of H-bridged systems, will be presented in a future publication.]

The 2-butyl cation was generated at Erlangen by using slight modifications of the Zagreb method,[9a–g] which refined and extended the earlier IR spectroscopic examinations of Olah[9a–b] and others.[9c,d] SbF_5 and 2-chlorobutane were co-deposited on the surface of a NaCl disc at −165 °C in a low temperature vacuum IR-cell. During warming to −60 °C a new peak at 2175 cm^{-1} appears. While this vanishes quickly at higher temperature, cooling to −125 °C just after the initial appearance of the peak, leads to the spectrum of the almost pure 2-butyl cation shown in Fig. 1(*b*), only slightly contaminated with the *tert*-butyl cation. Upon warming to −10 °C, the 2-butyl cation is rearranged completely to *tert*-$C_4H_9^+$ (the spectrum has already been reported by Olah[9a]). The peak at 2175 cm^{-1} in Fig. 1(*b*) provides striking evidence for H-bridging (Table 1). The significant observed experimental frequencies can be fit with values calculated for **1**: a graphical comparison is shown in Fig. 2. The agreement (correlation coefficient cc = 0.9995) could hardly be better! Since the frequencies are calculated using the harmonic approximation, a slope $m = 0.945$ is found as expected.[5,17] Table 2 compares the calculated frequencies for **1** and **2** (scaled by 0.94) and the experimental data. The H-bridged form **1** is the main species in our SbF_5 matrix. Although there is no definite evidence for **2**, the presence of a small amount (up to *ca.* 20%) cannot be excluded.

As exemplified by **1**, 1,2-H-bridged carbocation structures are now firmly established. An alternative set of rapidly equilibrating unsymmetrical species is excluded by the $C(H\updownarrow)C$ frequency near 2100 cm^{-1} [see Table 1 and Figs. 1(*a*), (*b*)], which characterizes symmetrical H-bridging.

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