Predicted NMR Coupling Constants and Spectra for Ethyl Carbocation: A Fingerprint for Nonclassical Hydrogen-Bridged Structures

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The prototypical primary carbocation, $C_2H_5^+$, is not stable enough to be observed directly in superacid media.[1−3] As the $CD_3CH_2F-SbF_5$ complex undergoes rapid intramolecular hydrogen (as well as carbon and fluorine) scrambling, it is not possible to decide between a hydrogen-bridged or classical ground state structure (Figure 1, **I** and **II**). However, the lower adiabatic than vertical ionization energy of the ethyl radical indicates the bridged form to be ~5−9.5 kcal/mol lower in energy in the gas phase.[4,5] Theoretical investigations at more sophisticated *ab initio* levels[4,6] predict the bridged isomer to be ~6−8 kcal/mol more stable than the "classical" form. The latter serves as the transition structure (one imaginary frequency at correlated levels of theory) for hydrogen scrambling.[4,6]

In this communication, we employ correlated coupled cluster (CC) and MBPT methods to present NMR shifts and, particularly, the initial prediction of the coupling constants for **I** and **II**. This fills a void in the data for hydrogen-bridged carbocations of the protonated ethylene type and should assist experimental characterization of such species. For example, while the IR spectrum of the H-bridged 2-butyl cation has been observed in a low-temperature SbF_5 matrix,[7] rapid hydrogen scrambling precludes resolution of the NMR spectra.

All calculations use the ACES II[8] program system. Geometries are determined at the coupled-cluster singles and doubles (CCSD) level[9,10] using a triple-ζ, double polarization (TZ2P, spherical) basis set.[11] Harmonic vibrational frequencies are calculated by finite differences of analytically computed gradients. We obtain CCSD(T)[9,10] results at the critical geometries of the "classical" transition structure and bridged form, using an augmented polarized valence triple-ζ (cc-pVTZ, spherical) basis set.[12] The NMR chemical shifts use gauge-including atomic orbitals (GIAO) at the second-order perturbation theory (MBPT(2)) level[13] and a QZ2P (Cartesian) basis set for C(6s,4p,2d) and for H a (3s,2p) (polarization exponents are 1.39 and 0.46).[14] The calculated chemical shifts reproduce the gas phase experimental ^{13}C and ^1H NMR shifts of hydrocarbons with an error of less than 1 ppm.[15] The NMR spin−spin coupling constants are calculated with the equation of motion coupled-cluster singles and doubles (EOM-CCSD) method.[10,16,17] EOM-CCSD results have been reported for several systems and shown to average within 10% of the experimental NMR coupling constants.[17] In the present investigation we use two Cartesian Gaussian basis sets to assess convergence: the first is (4s,1p) for H and (6s,3p,1d) for C;[18] and the second is (5s,3p) for H (polarization exponents are 2.292, 0.838, and 0.292) and (8s,5p,2d) for C (polarization exponents are 1.39 and 0.46).[14] We include all four coupling mechanisms which contribute to the total spin−spin coupling constant: the Fermi contact (FC), spin−dipole (SD), paramagnetic spin−orbit (PSO), and diamagnetic spin−orbit (DSO) contributions. Since all coupling constants, total and components, differ by no more than 1.5 Hz, we only report the basis II values in Tables 3 and 4.

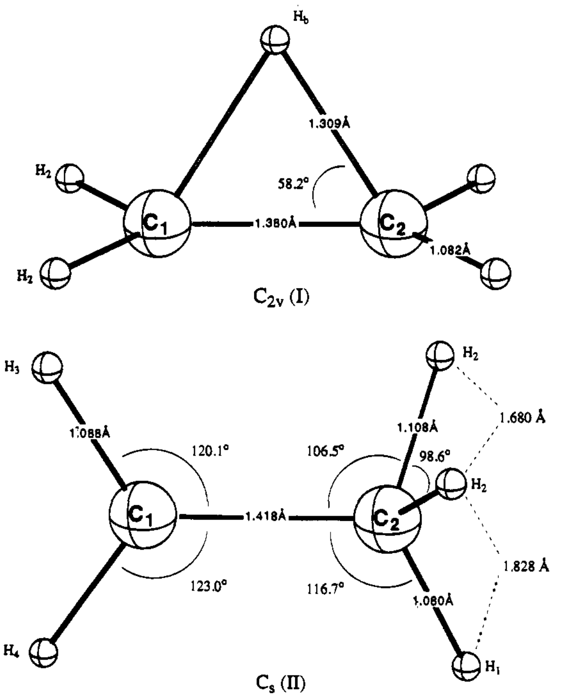

Figure 1. CCSD (TZP, spherical) optimized structures for bridged and "classical" forms of $C_2H_5^+$ used in NMR calculations.

The CCSD/TZ2P bridged (**I**) and "classical" (**II**) geometries are given in Table 1 and in Figure 1. The $H_2C_2H_2$ angle of only 98° and the relatively long (1.108 Å) C_2H_2 and short H_2⋯H_2 (1.68 Å) separation might be said to correspond to a three-center, two-electron bond arising from the hyperconjugative interaction of the "vacant" C(p) orbital with both hydrogens[19] somewhat similar to an H_2 complex of the vinyl cation, H_2CCH^+⋯H_2. Yet the H_2⋯H_2 distance has a much longer bond length than usual for H_2 (0.746 Å). A consequence of the structure is the unusually small $^1J(C_2H_2)$ coupling constant (109 Hz) computed for **II** (see Table 4).

These extremum points, **I** and **II**, on the $C_2H_5^+$ potential energy surface are characterized by the CCSD/TZ2P finite difference vibrational frequencies (full set available upon request). The perpendicular stretching vibration ($\omega_5(A_1)$) involving the bridging hydrogen in **I** is predicted to give rise to

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Table 1. Ground State Equilibrium Geometries of the "Classical" Transition Structure and Bridged Forms of the $C_2H_5^+$ Cation[a]

	C_{2v} (I)	C_s (II)		C_{2v} (I)	C_s (II)
C_1C_2	1.380 23	1.418 18	$H_2C_1H_2$	119.050 99	
C_1H_b	1.309 42		$H_2C_2H_2$		98.610 09
C_2H_1		1.079 99	$H_2C_1H_b$	105.666 90	
C_1H_2	1.081 87		$H_2C_2H_1$		113.336 86
C_2H_2		1.108 13	$H_1C_2C_1$		116.746 16
C_1H_3		1.085 64	$H_4C_1C_2$		122.968 05
C_1H_4		1.085 90	$H_3C_1C_2$		120.058 34

[a] The reported results are CCSD/TZ2P optimized geometries. Bond lengths are in angstroms, and bond angles are in degrees. For CCSD(T), $E(I) = -49\,403.0694$ kcal/mol and $E(\mathbf{II}) = -49\,410.2358$ kcal/mol.

Table 2. GIAO-MBPT(2)/QZ2P NMR Chemical Shifts (δ, in ppm) of the "Classical" Transition Structure and Bridged Form of the $C_2H_5^+$ Cation[a]

	C_{2v} (I)	av (I)	C_s (II)	av (II)		C_{2v} (I)	av (I)	C_s (II)	av (II)
C_1	163.97	163.97	361.17	217.57	H_2	7.89	6.31	5.26	8.54
C_2			73.96		H_3			13.56	
H_b (H_1)	−0.02		5.16		H_4			13.47	

[a] The reported chemical shifts are relative to TMS as the reference. The ^{13}C and ^1H shieldings for ethylene are 133.60 ppm (MBPT(2)/QZ2P) and 5.21 ppm (MBPT(2)/QZ2P), respectively.

Table 3. NMR Spin−Spin Coupling Constants of $C_2H_5^+$ for the Bridged Form (in Hz)

coupling	FC	SD	PSO	DSO	total
$^1J(C_1H_b)$	10.23	−0.08	2.30	0.56	13.01
$^2J(H_bH_2)$	−8.58	0.10	1.83	−1.70	−8.52
$^1J(C_1H_2)$	166.64	0.45	−0.75	0.32	166.66
$^3J(H_2H_2)_{cis}$	8.31	0.00	0.77	−1.06	8.02
$^3J(H_2H_2)_{trans}$	17.72	0.05	3.04	−3.53	17.28

Table 4. NMR Spin−Spin Coupling Constants of $C_2H_5^+$ for the "Classical" Transition Structure (in Hz)

coupling	FC	SD	PSO	DSO	total
$^1J(C_1H_3)$	162.87	1.04	−3.17	0.10	160.84
$^1J(C_1H_4)$	161.49	1.15	−3.09	0.09	159.64
$^1J(C_2H_1)$	151.43	0.18	0.38	0.45	152.44
$^1J(C_2H_2)$	107.19	0.05	1.17	0.51	108.92
$^3J(H_1H_4)$	9.65	0.12	0.76	−0.97	9.56
$^3J(H_1H_3)$	15.89	0.00	2.85	−3.40	15.34
$^3J(H_2H_3)$	−1.85	0.14	0.92	−1.05	−1.84
$^3J(H_2H_4)$	−0.02	0.09	2.51	−2.85	−0.27

an intense signal at 2186 cm^{-1} in an unusual region of the IR spectrum. A similar feature (at 2175 cm^{-1}) has been observed for the 2-butyl cation.[7] The transition structure for H-scrambling, **II** ($\omega_{15}(A'')$), has a rather large imaginary frequency (369i), corresponding to a complex twisting motion.[4,6] Our $\Delta^{\ddagger}H^{\circ}$ (including zero-point vibration, 0 K) barrier predictions, 6.9 and 8.1 kcal/mol at CCSD and CCSD(T), respectively, at the CCSD/TZ2P geometries, are at the highest levels which have been reported to date.

The computed chemical shifts of H_2 (7.89) and C_1 (163.97) of bridged $C_2H_5^+$, relative to TMS, may be compared with the ^1H and ^{13}C chemical shifts computed for ethylene, 5.21 and 133.60, respectively. (The gas phase experimental C_2H_4 values are 5.08 and 133.88.[20]) The chemical shift (−0.02) of the bridging hydrogen, H_b in **I**, is unexceptional. The charges on such bridging H's are similar to those of the other hydrogens.[21] Table 2 also summarizes the average ^1H and ^{13}C chemical shifts, which might result from complete scrambling, assuming **I** or **II** were the only populated forms. These quite different values demonstrate how easily they could be distinguished, in principle. Of course, the individual H and C chemical shifts computed for **II** vary considerably.

The EOM-CCSD NMR spin−spin coupling constants (Tables 3 and 4) show that $^1J(C_1H_b) = 13$ Hz for **I**. This is an unusually small value as ^1J(CH) values in hydrocarbons generally range between 125 and 250 Hz, with the ethylene value being 156 Hz;[22] the 13 Hz coupling constant should provide a fingerprint for such 1,2-hydrogen-bridged nonclassical cations. Unsupported μ-H-bridged (C−H−C) carbocations are known that have consistent ^1J(CH) values, in the 35−40 Hz range,[7,23] although lower values have been measured in more weakly bonded unsymmetrical systems.[24] The $^1J(CH) = 166.7$ Hz, computed for nonbridging H's of **I**, is 10.7 Hz larger than the ethylene value. As the FC component dominates the coupling, the bond polarization which increases ^1J(CH) exceeds the lowering effect caused by the hybridization change from sp^2 to sp^3.

The accuracy of EOM-CCSD is monitored by calculating the NMR spin−spin coupling constants of cyclopropane, methane, and ethylene. The computed versus experimental ^1J(CH) coupling constants are 154 (161),[25] 117 (121),[26] and 148 (156),[22] respectively. The calculated ^1J(HD) of CH_3D, −2.15, compares to −1.93.[26] Furthermore, the $^2J(HH)$, $^3J(HH)_{trans}$, and $^3J(HH)_{cis}$ proton−proton coupling constants of ethylene are −1.4 (2.5), 15.1 (19.1), and 10.0 (11.6), respectively.[22]

To further establish the accuracy of our prediction for $^1J(CH_b)$ involving the bridged hydrogen, we apply the same EOM-CCSD method to diborane in a comparable basis. There we obtain 43.4 Hz for $^1J(^{11}BH_b)$, compared to a 43 Hz experiment.[27] Similarly, $^1J(^{11}BH_t)$ is 123.5 Hz compared to 125 Hz.[30]

Olah et al.[2] observed that SbF_5 complexation of CH_3CH_2F led to a ca. 12 Hz increase in the α ^1J(CH) to 162 Hz, but only to slight deshielding of the α ^{13}C and ^1H chemical shifts. Comparing these results with our predictions of the "classical" ethyl cation (**II**) magnetic properties (Tables 2, 4), the chemical shifts computed for C_1 (the carbenium carbon) as well as the attached hydrogens, H_3 and H_4 (Table 2), are all highly deshielded, consistent with experimental observations, e.g., for the 2-propyl cation.[1] Also, the computed $^1J(C_1H_3)$ and $^1J(C_1H_4)$ values are both near 160 Hz. It is apparent, though, that the $CH_3CH_2F-SbF_5$ complex has little bridged carbenium ion character.

Comparisons between computed and experimental NMR chemical shifts have become a powerful tool for structure elucidation.[15,28] Accurate computations of NMR coupling constants,[17] as illustrated here, and which can be obtained regardless of the atoms involved, will greatly extend the applicability of such theoretical predictions.

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