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Structure and NMR Spectra of the 2-Norbornyl Carbocation: Prediction of $^{1}J(^{13}C^{13}C)$ for the Bridged, Pentacoordinate Carbon Atom

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The structure of the 2-norbornyl cation (Figure 1) has been the focal point of one of the primary controversies in physical organic chemistry.[1−3] Over the last 40 years, a large number of experimental and theoretical investigations have attempted to establish whether the classical (Figure 1, I) or the nonclassical structure (Figure 1, II) is more stable (or even exists?).

The experimental evidence, based on a variety of spectroscopic techniques,[4−11] with NMR the most prominent, favors the symmetric bridged (nonclassical) structure for the 2-norbornyl cation in nonnucleophilic media, where direct spectroscopic measurements can be made. First, Schleyer and Chandrasekhar (SC) conclude that the 2-norbornyl cation has an extra stabilization of 6−15 kcal/mol due to bridging in stable ion media.[12,13] This extra stabilization might be due to some factors other than bridging, but, as SC point out, the experimental evidence favoring the bridged structure of the 2-norbornyl cation is now overwhelming.

The principal tool used to establish the nonclassical bridged form, which contains a pentacoordinate carbon, has been NMR. In particular, it is not possible to directly observe the coupling constants involving the pentacoordinated carbon even with a ^{13}C-enriched molecule. Yet, as stated in Jarret and Saunders,[11] "in particular, special properties of the interesting pentacoordinated bridging carbon, are of special interest". Consequently, we use our recently developed EOM-CCSD method to predict these coupling constants. Before doing so, however, we must obtain the structure of the carbocation.

A number of semiemperical and *ab initio* theoretical studies of the energetics of various structures of the 2-norbornyl cation have been previously presented, but, except for ref 15, typically not at predictive levels. See ref 14 for a review. The best previous calculations optimized the geometry at the MBPT(2) level with a 6-31G* basis.[14,15]

Here, we employ DZP basis sets (more flexible than 6-31G*) combined with MBPT(2) in geometry optimizations and at the coupled cluster singles and doubles (CCSD) level in single-point energy calculations. We provide the NMR chemical shifts using gauge-including atomic orbitals (GIAO-MBPT(2))[16,17] and the spin−spin coupling constants using EOM-CCSD methods[18−20] for the optimum structure of the 2-norbornyl cation. This provides, in particular, results for the $^{1}J(^{13}C^{13}C)$ coupling constants for the bridged pentacoordinated C, which are not experimentally available.

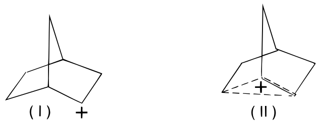

Figure 1.

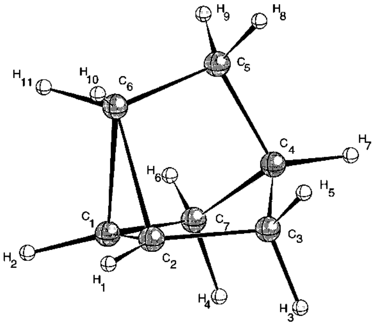

Figure 2. MBPT(2)/DZP geometry of the nonclassical form of the 2-norbornyl cation. $r(C_6C_5) = 1.530\,40$ Å, $r(C_5C_4) = 1.539\,42$ Å, $r(C_4H_7) = 1.093\,89$ Å, $r(C_5H_8) = 1.095\,18$ Å, $r(C_1H_{10}) = 1.098\,87$ Å, $r(C_1C_6) = 1.832\,63$ Å, $r(C_1H_2) = 1.090\,35$ Å, $r(C_3C_4) = 1.541\,20$ Å, $r(C_7H_6) = 1.095\,26$ Å, $r(C_7H_4) = 1.100\,58$ Å, $\alpha(C_6C_5C_4) = 100.834\,96°$, $\alpha(C_5C_4H_7) = 115.727\,23°$, $\alpha(C_4C_5H_8) = 112.310\,48°$, $\alpha(C_5C_6H_{10}) = 117.511\,81°$, $\alpha(C_2C_6H_5) = 102.832\,63°$, $\alpha(C_6C_1H_2) = 110.169\,42°$, $\alpha(C_7C_4H_7) = 115.623\,91°$, $\alpha(C_4C_7H_6) = 114.511\,34°$, $\alpha(C_4C_7H_4) = 112.432\,23$, $\tau(H_8C_5C_4H_7) = 61.746\,91°$, $\tau(H_{10}C_6C_5C_4) = 116.128\,71°$, $\tau(C_2C_6C_5C_4) = 23.102\,84°$, $\tau(H_2C_1C_6C_5) = 145.632\,73°$, $\tau(C_{13}C_4C_3C_2) = 120.390\,01°$, $\tau(H_6C_7C_4H_7) = 68.572\,00°$, $\tau(H_4C_7C_4H_7) = 56.860\,67°$.

All calculations use the ACES II program system.[21] Geometries are determined at the SCF and MBPT(2) levels using a standard DZP basis set comprised of (9s,5p,1d)/[4s,2p,1d] contraction for C and (4s,1p)/[2s,1p] contraction for H.[22,23] The basis sets employed in NMR calculations are described in the footnotes of Table 2.

The MBPT(2)/DZP geometry of the nonclassical form is depicted in Figure 2; it is a true minimum on the potential energy surface with C_s symmetry as was shown by the SCF/DZP and MBPT(2)/DZP vibrational frequency calculations.[24] Any attempt to obtain the MBPT(2)/DZP optimized geometries for the classical form from a starting geometry which resembles the classical form with C_1 symmetry fails since the final optimized geometry corresponds to the nonclassical structure. This shows that in the gas phase there is no energy barrier at the MBPT(2)/DZP level between the nonclassical and the classical forms, making the stable structure exclusively nonclas-

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(24) The vibrational frequencies are available upon request.

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Table 1. GIAO-MBPT(2) NMR Chemical Shifts (δ, in ppm) of the Nonclassical 2-Norbornyl Cation[a]

	chemical shift	expt[b]		chemical shift	expt[b]
C_6	22.92	21.2	H_8, H_9	1.22	1.37
C_5	24.81	20.4	H_{10}, H_{11}	2.48	3.17
C_4	40.44	37.7	H_1, H_2	6.34	6.75
C_1, C_2	121.79	124.5	H_5, H_6	2.07	2.13
C_3, C_7	40.97	36.3	H_3, H_4	2.03	2.13
H_7	2.95	2.82			

[a] The GIAO-MBPT(2) NMR chemical shifts are calculated at the MBPT(2)/DZP optimized geometry employing a DZP basis on C atoms and a DZ basis on hydrogen atoms. The reported chemical shifts are relative to TMS as the reference. The GIAO-MBPT(2)/DZP NMR chemical shifts of TMS at the MBPT(2)/DZP optimized geometry are δ^{13}C 204.77 and δ^{1}H 31.53. The spherical harmonic Gaussian basis has been used in geometry optimizations, vibrational frequency, and single-point energy calculations, while Cartesian Gaussian basis functions have been used in NMR chemical shifts and spin−spin coupling constant calculations. [b] G. A. Olah *et al.*[7]

Table 2. EOM-CCSD NMR Spin−Spin Coupling Constants of the Nonclassical 2-Norbornyl Cation (in Hz)[a]

coupling	EOM-CCSD	average	expt
${}^1J(C_2H_1)$, ${}^1J(C_1H_2)$	175.4 (177.2)		187.7[b]
${}^1J(C_6H_{11})$, ${}^1J(C_6H_{10})$	138.4 (140.4)		147.1 ± 5[b]
${}^1J(C_7H_6)$, ${}^1J(C_3H_5)$	133.9 (135.3)		131.2[b]
${}^1J(C_7H_4)$, ${}^1J(C_3H_3)$	125.2 (126.7)		
${}^1J(C_5H_9)$, ${}^1J(C_5H_8)$	130.6 (132.0)		153.2 ± 5[b]
${}^1J(C_4H_7)$	144.5 (145.9)		150.9[b]
$J(H_1H_7)$, $J(H_2H_7)$	0.4 (−1.1)	0.4 (−1.2)	0.4[b]
$J(H_{11}H_7)$, $J(H_{10}H_7)$	0.0 (−1.2)		
$J(H_6H_7)$, $J(H_5H_7)$	1.0 (0.5)	1.6 (1.3)	1.6[b]
$J(H_4H_7)$, $J(H_3H_7)$	2.2 (2.0)		
$J(H_2H_6)$, $J(H_1H_5)$	1.9 (1.5)	0.9 (0.0)	1.4[b]
$J(H_2H_4)$, $J(H_1H_3)$	0.3 (−0.4)		
$J(H_{11}H_6)$, $J(H_{10}H_5)$	−0.3 (0.0)		
$J(H_{11}H_4)$, $J(H_{10}H_3)$	0.9 (−0.2)		
$J(H_{11}H_3)$, $J(H_{10}H_4)$	5.4 (4.2)		
$J(H_{11}H_5)$, $J(H_{10}H_6)$	0.2 (−1.0)		
$J(H_2H_5)$, $J(H_1H_6)$	−0.1 (−1.5)		
$J(H_2H_3)$, $J(H_1H_4)$	−0.8 (−1.9)		
${}^1J(C_5C_4)$	28.7 (28.5)	29.8 (29.5)	29.4[c]
${}^1J(C_4C_7)$, ${}^1J(C_4C_3)$	30.3 (30.0)		
${}^1J(C_5C_6)$	37.7 (37.0)	36.0 (34.8)	33.0[c]
${}^1J(C_1C_7)$, ${}^1J(C_2C_{C3})$	35.2 (33.7)		
${}^1J(C_1C_2)$	41.8 (35.1)		
${}^1J(C_1C_6)$, ${}^1J(C_2C_6)$	−5.6 (−4.5)		

[a] The EOM-CCSD NMR spin−spin coupling constants at the MBPT(2)/DZP optimized geometry. The results given in parentheses include noncontact contributions. The FC contributions are calculated by employing a DZP basis on C atoms and a DZ basis on H atoms. The noncontact contributions are calculated by using a DZ basis. [b] G. A. Olah *et al.*[7] [c] M. Saunders *et al.*[11]

sical. This is contrary to what previously has been reported in the literature[25] (see ref 14 for a review). However, the existence of the classical form as a stationary point in previous theoretical calculations appears to have been an artifact of inadequate basis set and correlation. Further support for this argument comes from the fact that we have been able to characterize classical structures by SCF/STO-3G and SCF/DZ geometry optimizations. In the following NMR calculations, we only consider the nonclassical structure with the MBPT(2)/DZP optimized geometrical parameters.

Tables 1 and 2 present the GIAO-MBPT(2) NMR chemical shift and EOM-CCSD NMR coupling constants of the nonclassical 2-norbornyl cation. The calculated NMR chemical shifts of the nonclassical form are in good agreement with the experimentally measured NMR chemical shifts of the 2-norbornyl cation at −158 °C in $SbF_5/SO_2ClF/SO_2F_2$ solution.[7] Observation of the C_1 and C_2 carbon ^{13}C chemical shifts of about 125 and C_6 chemical shift of about 20−30 supports a symmetrical bridged structure for the 2-norbornyl cation since five (or higher coordinate) carbons usually show shielded (upfield) ^{13}C chemical shifts.[26−28] The absence of highly deshielded (downfield) carbon atoms, a characteristic of the trivalent sp^2 carbon atoms, as occurs for example in *tert*-butyl cation and cyclopentyl cation,[29] also supports the bridged nature of the 2-norbornyl cation.

It is well-known in the literature[20] that the significance of noncontact contributions for the $J(^{13}C^{1}H)$ and $J(^{13}C^{13}C)$ coupling constants of hydrocarbons is slight, and also the noncontact contributions are relatively less sensitive to the basis set compared to the FC contribution. Hence, we focus on the FC contribution to the NMR spin−spin coupling constants and provide an estimate of the noncontact contributions using smaller basis sets.

As we can see from Table 2, calculated NMR spin−spin constants are in good agreement with the experimentally measured ones.[7] This further supports Olah's claim that the experimentally measured NMR spectrum corresponds to the nonclassical form of the 2-norbornyl cation. Consequently, the symmetric bridged form of the 2-norbornyl cation exists as a long lived species in superacid medium at low temperatures. The usual ${}^1J(^{13}C^{13}C)$ coupling constants are in the range of +10−40 Hz. However, in Table 2, the ${}^1J(^{13}C_6{}^{13}C_1)$ and ${}^1J(^{13}C_6{}^{13}C_2)$ coupling constants of pentacoordinated bridged carbon atom (C_6) to bridge head carbon atoms (C_1 and C_2) are negative and have a smaller magnitude. This characteristic is associated with other bicyclic molecules[30] and is often attributed to interference between one-bond and two-bond couplings. This can be used as a fingerprint to identify penta- (or higher) coordinated bridged carbon structures. As we can see from Table 2, the effect of the noncontact contributions is insignificant (about 1 Hz) for $J(^{13}C^{1}H)$ and $J(^{13}C^{13}C)$ coupling constants. However, some of the $J(^{1}H^{1}H)$ coupling constants presented in Table 2 have significant noncontact contributions, but the overall magnitude of these coupling constants is small.

In the case of theoretical NMR spectroscopy, the structure responsible for the calculated NMR spectrum is known a priori. On the other hand, in the case of experimental NMR spectroscopy, the molecular structure responsible for the NMR spectrum has to be inferred from the measured spectrum. The agreement shown in Tables 1 and 2 of the calculated NMR parameters of the nonclassical 2-norbornyl cation with the experimentally measured NMR parameters at −158 °C argues against the possible presence of the classical structure. This is a perfect illustration of employing calculated NMR parameters for conclusive correlations of the measured spectrum with the molecular structure. We predict that ${}^1J(^{13}C_6{}^{13}C_1)$ has a small value of −4 to −6 Hz which is indicative of the bridged pentacoordinate structure.

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