The Accurate C_{2v} Phenonium and Benzenonium Ion Structures Confirmed by Correlated GIAO-MP2 NMR Chemical Shift Calculations

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Cram presented the first evidence for the intermediacy of phenonium ions in the solvolysis of β-arylalkyl halides in 1949.[1,2] This cornerstone of the theory of anchimeric assistance[3,4] was questioned in 1962 by H. C. Brown.[5] Although his doubts could be resolved six years later,[6] the accurate molecular structures of the phenonium ion (**1**)[7] as well as that of the closely related benzenonium ion[8] (protonated benzene, **2**) still have not been determined experimentally. We have now employed a new development, the ability to compute NMR chemical shifts at the correlated GIAO-MP2 level,[9] to establish the reliability of the MP2/6-31G* ab initio geometries.

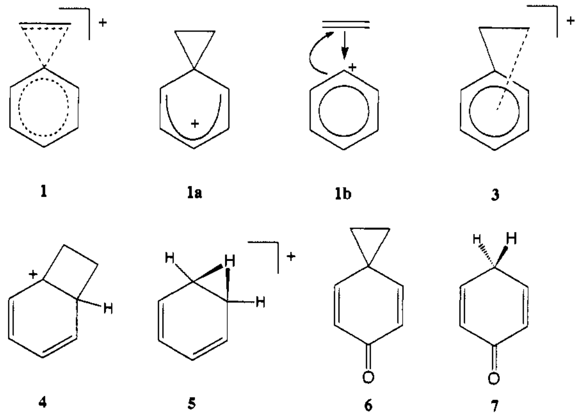
While Olah's NMR characterization of the parent phenonium ion **1**[7] (as well as **2**)[8] under stable ion conditions points to C_{2v} symmetry (or time-averaged C_{2v} symmetry), a wide spectrum of formulations—ranging from the "classical" spiro hexadienyl cation (**1a**)[10] to the phenyl cation–ethylene π-complex (**1b**)[11]—have been proposed. Köppel and McLafferty claim that a protonated benzocyclobutene (**4**), rather that **1**, forms by ionization of β-phenylethyl derivatives in the gas phâse.[12] Earlier ab initio computations on **1**, carried out only at minimal basis set (STO-3G) levels without frequency analysis,[13] indicated **1** to be more stable than open β-phenylethyl cation forms and also the "planar tetracoordinate carbon" alternative.[14]

Table I. Comparison of Calculated and Experimental ^{13}C NMR Chemical Shifts of the Phenonium Ion **1** and the Benzenonium Ion **2** (ppm vs TMS)

species	method	C^1	C^2	C^3	C^4	C^7
1	IGLO/DZ[a]	46.6	182.8	131.8	171.2	55.7
	IGLO/II[b]	57.8	189.3	137.4	177.1	53.1
	GIAO-SCF/TZP/DZ[c]	54.6	185.7	133.6	173.5	50.0
	GIAO-MP2/TZP/DZ[c]	71.9	168.1	140.8	153.6	61.5
	expt[d]	68.8	171.8	133.4	155.4	60.7
2	IGLO/DZ[a]	39.9	196.4	131.9	189.9	
	IGLO/II[b]	39.2	197.4	131.8	194.8	
	GIAO-SCF/TZP/DZ[c]	41.5	198.7	132.8	196.6	
	GIAO-MP2/TZP/DZ[c]	52.5	185.3	141.3	176.0	
	expt[e]	52.2	186.6	136.9	178.1	

[a] IGLO/DZ values are vs CH_4 (correction for TMS is ≈0). [b] IGLO/II values are corrected for TMS by −5.7 ppm. [c] TZP/DZ: polarized (α = 0.8) triple-ζ basis for carbon (51111/311/1), double-ζ basis for hydrogen (31), cf.: Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. The calculated absolute shieldings for TMS are 193.1 (GIAO-SCF/TZP/DZ) and 198.9 ppm (GIAO-MP2/TZP/DZ), respectively. [d] Reference 7. [e] Reference 8.

Scheme I



Our extensive theoretical investigation of the accurate molecular structures and energies of carbocations[15] have included $C_6H_7^+$ and $C_8H_9^+$ species. The validity of, e.g., MP2/6-31G* geometries, is established by comparing the computed NMR chemical shifts and, more recently, vibrational frequencies[15h–j] against the experimental data. While the combined *ab initio*[16]/IGLO[15d,17]/NMR structural method has been applied to a variety of carbocations with considerable success,[15] the errors between the computed and the experimental shifts of **1** (and **2**) with IGLO (Table I) were unacceptably large. Even the larger IGLO basis

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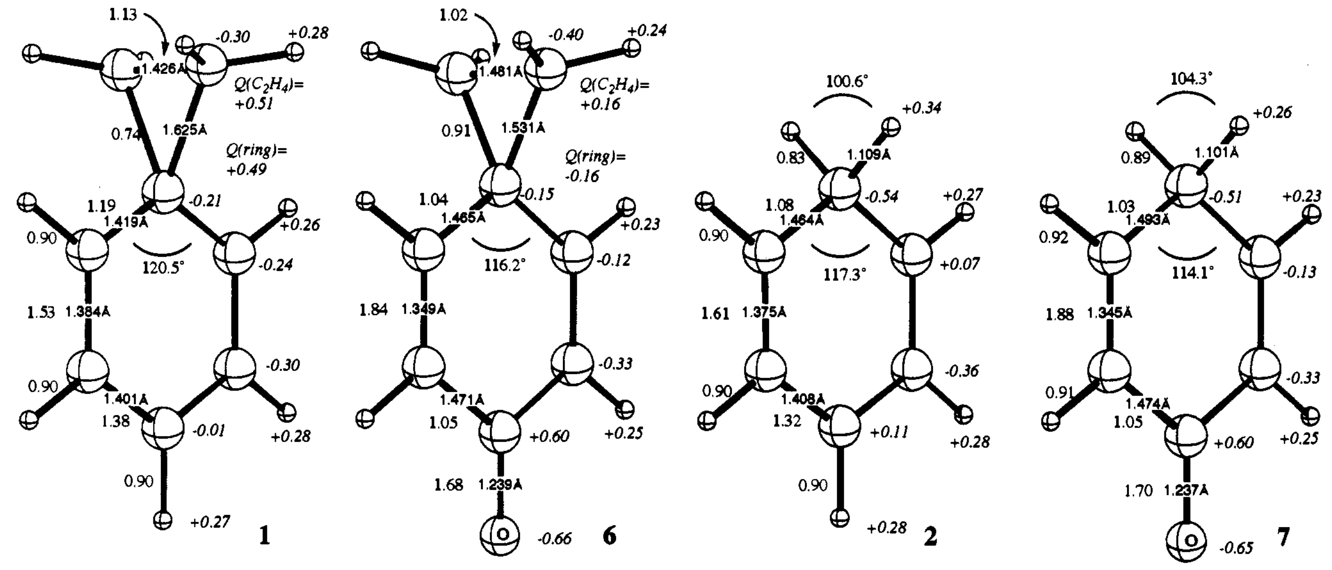

Figure 1. MP2/6-31G* optimized structures of the phenonium ion **1**, spiro[5.2]octa-2,5-dien-4-one **6**, the benzenonium ion **2**, and cyclohexa-1,4-dien-3-one **7**; NPA charges (in italics) and Wiberg bond orders are computed at HF/6-31G*//MP2/6-31G*.

II (of near triple-ζ plus polarization (TZP) quality), known to perform better in critical cases,[18] showed no improvement over the standard double-ζ (DZ) basis. Disturbed by the discrepancies between computed and experimental ^{13}C NMR chemical shifts, we explored alternative structural possibilities for **1** (and **2**) at correlated levels of ab initio theory and searched for additional minima with reduced or with no symmetry (see Scheme I).

Both C_s and C_2 starting geometries of **1** and **2** with nonplanar and twisted rings return upon optimization back to the higher symmetry C_{2v} forms. A partially bridged form **3**, suggested by Brown et al.,[5,19] relaxed to **1** or, with larger initial distortions, led to McLafferty's structure **4** (a minimum, but substantially higher in energy than **1**).[12] This alternative also was excluded by the large deviations of the computed ^{13}C chemical shifts for **4** (assuming rapid hydrogen migrations and effective C_{2v} symmetry). Widely cast searches for additional minima related to **1**, without imposing any symmetry constraints (C_1), were unsuccessful. The C_{2v} structures of **1** and **2**, shown in Figure 1, are the only minima in the adjacent region of their respective potential energy surfaces. The possible presence of a mixture of **1** and **4** was checked by interpolating the computed chemical shifts. Again the observed values could not be reproduced. The symmetrically H-bridged structure **5** was confirmed to be the transition state for H-migration of the benzenonium ion **2**. Both the computed barrier (7.9 kcal mol^{-1}) and the proton affinity (182.1 kcal mol^{-1}, based on **2**)[20] agreed well with the experimental values, 8.0[8] and 181.3[21] kcal mol^{-1}, respectively.

Both in **1** and **2** the major deviations of the IGLO chemical shifts from experiment are for carbons C^1, C^2, and C^4 (Table I). The recently developed GIAO[22]-MP2 (or GIAO-MBPT(2)) method[9] includes correlation effects in practicable chemical shift calculations for the first time. Application of GIAO-MP2 to **1** and **2** was decisive! Using a triple-ζ plus polarization basis set (TZP) for carbon and a double-ζ basis (DZ) for hydrogen (comparable to the IGLO basis sets II for C, DZ for H) the experimental data are finally reproduced well. The average errors of 12.4 ppm for **1** and 11.4 ppm for **2** (IGLO/II) are reduced greatly to 3.3 and 2.0 ppm, respectively (Table I). Since the errors at the GIAO-SCF level are similar to those of the IGLO calculations, the earlier difficulties in fitting the theoretical with the experimental NMR data are due to the lack of inclusion of correlation effects and not to inadequate geometries. Preliminary calculations on the naphthalenium and anthracenium ions indicate that similar errors in the computed chemical shifts at SCF levels are systematic in protonated aromatic hydrocarbons. In substituted allyl cations, similar errors at SCF[17c] also are corrected with GIAO-MP2.[23]

Figure 1 compares the geometries and electronic structures of **1** and **2** with the corresponding ketones, **6** and **7** (taken as classical bonding models). The bond length variations, natural charges,[24] and Wiberg bond orders from NBO analysis[24] are instructive. Both ketones **6** and **7** have the expected classical, quinonoid structures. However, some hyperconjugative involvement of the three-membered ring is apparent in **6** (note the difference in bond lengths and orders). The benzenonium ion **2** also shows some hyperconjugative participation of the CH_2 group in quasi 6π aromaticity (small HCH angle, increased C^1–C^6 bond order, and decreased C^1–C^6 length vs **7**), but the conjugated dienyl cation character dominates. The phenonium ion structure is significantly different. *Half* the positive charge is delocalized to the two CH_2 groups. The CC bond lengths in the six-ring are nearly equal (1.401 ± 0.018 Å) but in the three-ring differ by 0.2 Å (1.426 vs 1.625 Å).[25] Hence, the phenonium ion is *nonclassical* with considerable 6π aromatic character and is most clearly represented by **1**.

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