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Quantum chemical calculation of structures and NMR chemical shifts of substituted buta-1,3-dienyl-2-cations†

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ABSTRACT: A computational study of ^{13}C NMR chemical shifts of a series of α-vinyl substituted vinyl cations (1,3-dienyl-2-cations) **1**–**6** is presented. The sensitivity of the predicted isotropic shifts to electron correlation, basis set and geometry effects is explored. Comparison with experimental ^{13}C NMR chemical shifts shows that second-order Møller–Plesset perturbation theory calculations [GIAO-MP2/tzp//MP2/6–31G(d,p)] perform adequately (deviation ≈ 3–4 ppm) for all carbons of cations **1**–**6**, except for carbons in **6** involved in cyclopropyl hyperconjugation, which give some larger deviations (≈ 6–9 ppm). The Hartree–Fock self-consistent field (GIAO-HF/tzp) approximation as well as GIAO-DFT-methods together with hybrid functionals (B3LYP) give unsatisfactory results and cannot be relied upon to predict the sequence of signals in the ^{13}C NMR spectra of these type of carbocations. Copyright © 2004 John Wiley & Sons, Ltd.
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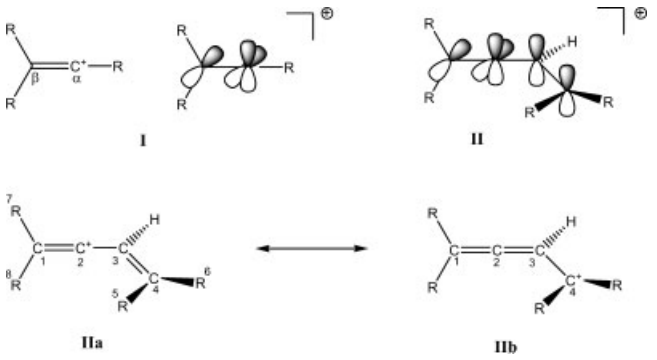
KEYWORDS: carbocations; vinyl cations; ^{13}C NMR chemical shift; quantum chemical calculations; GIAO-HF; GIAO-DFT; GIAO-MP2

INTRODUCTION

Vinyl cations (**I**) are well-established reactive intermediates.[1–3] A number of stabilized vinyl cations are accessible as long-lived species in solution and have been studied by ^{13}C NMR spectroscopy.[4–15] Vinyl cations (**I**) have a formally vacant p-orbital at the C$^+$-carbon Cα which is orthogonal to a non-interacting Cα–Cβ double bond. 1-Vinyl substituted vinyl cations (1,3-dienyl-2-cations, **II**) are stabilized by 2p-π-conjugation between the formally vacant 2p^z-orbital at C2 and the C3–C4 allylic double bond. In the parlance of valence bond theory dienyl cations **II** can be described as a hybrid of resonance limiting structures, the α-vinyl vinylcation (1,3-dienyl-2-cation, **IIa**) and the allenylmethyl cation (1,2-dienyl-4-cation, **IIb**).



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Calculations of NMR chemical shifts have become routine only recently.[16–23] The successful prediction of experimental NMR chemical shifts of carbocations was an important contribution to the recognition of NMR computations as a significant and potential structural tool.[24–27] The combined approach of experiments and computations has evolved into a standard tool in carbocation chemistry and related fields.

Despite the successful prediction of chemical shifts for a great structural variety of carbocations some difficulties have been encountered for vinyl cations.[13,28] The effect of electron correlation, basis sets and geometry on calculated NMR spectra of vinyl cations has been studied in some detail.[29] Comparative experimental and computational studies, however, have been reported for only two vinyl cation structures.[13,15] These studies have shown a congruence of CCSD(T)/tzp/dz calculated and observed ^{13}C NMR chemical shifts ($\Delta \approx$ 1–2 ppm), which suggests that the geometry of vinyl cations in superacid solution is similar to the gas phase and that the ^{13}C NMR chemical shifts are more or less unperturbed by interaction with the medium. This is in accord with the fact that weakly coordinating anions[30] such as SbF_5X^-, $Sb_2F_{10}X^-$ (X = Cl) and higher oligomeric anions, which are present in superacid solutions containing a large excess of SbF_5, exhibit a very low nucleophilicity and thus no site specific solvation.

In this paper we compare computational and experimental ^{13}C NMR spectra of a range of substituted vinyl cations in the investigation of the effect of substituents on structure and chemical shift in more detail. For the

substituted dienyl cations **1–6** we show that the combined *ab initio* GIAO-MP2 NMR[31,32] approach leads to good agreement with experiment, provided that electron correlation is included in the geometry optimization and the chemical shift calculation.

RESULTS AND DISCUSSION

The vinyl cations **1–6** (Scheme 1) have been characterized experimentally by ^{1}H and ^{13}C NMR spectroscopy in superacid solution.[6,8,15,33,34]

For the smaller systems, the *Z*-penta-1,3-dienyl-2-cation (**1**) and the *E*-penta-1,3-dienyl-2-cation (**2**) very high level quantum chemical calculations of the NMR chemical shifts up to the CCSD and CCSD(T) level [35,36,37] with a tzp basis for carbon and a dz basis for hydrogen have been reported.[15] These data demonstrated the importance of electron correlation effects for NMR chemical shift calculations of vinyl cations. In this study we extend the comparison of calculated and experimental NMR chemical shifts including **1** and **2** to higher substituted vinyl cations, the 4-methylpenta-1,3-dienyl-2-cation (**3**), the 5-methylhexa-2,4-dienyl-3-cation (**4**), the 2,5-dimethyl-2,4-dienyl-3-cation (**5**) and the1-(2′-methyl)propenyl-cyclo-propylidenemethyl cation (**6**). Owing to the larger size of these molecules, the high computational cost and the somewhat limited availability of CC-NMR–methods for this comparative study we consider only the less expensive second-order Møller–Plesset perturbation theory (GIAO-MP2) approach for electron correlation.

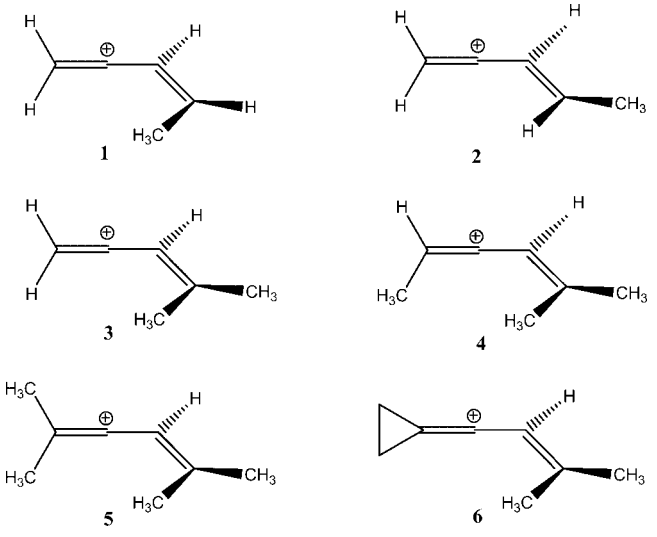
Geometries

The geometries for cations **1–6** were optimized using the Hartree–Fock self-consistent field approximation [HF/6–31G(d,p)], the DFT method together with the hybrid functional [B3LYP/6–31G(d,p)], and a second-order perturbation theory treatment [MP2/6-31G(d,p)]. All structures were confirmed to be minima. Some model calculation were performed for **1**, **5** and **6** with MP2 electron correlation including diffuse functions and larger basis sets such as 6–31+G(d,p), tzp, 6–311G(d,p) and 6–311+G(d,p) (see Tables **S1–S3** in the Supplementary Material). For a description of the MP2 method and the Gaussian basis sets, see for example Ref. 38, and Ref. 39 for a description of the tpz basis set. The differences in bond distances observed are generally small (< 0.01 Å). For the carbon framework of **1**, for example, marginally shorter bond distances were calculated at MP2/tzp level as compared with MP2/6–31G(d,p) [Δr(C1–C2) = 0.009 Å, Δr(C2–C3) = 0.007 Å, Δr(C3–C4) = 0.005 Å, Δr(C4–CH_3) = 0.005 Å]. We therefore concluded that the MP2/6–31G(d,p) geometries are sufficiently accurate for our comparative study of **1–6**. The sufficient convergence of the MP2/6–31G(d,p) geometries with respect to the wave function model was confirmed by GIAO-MP2/tzp NMR calculation of **1**, **5** and **6** for MP2 geometries with 6–31+G(d,p), tzp, 6–311G(d,p) and 6–311+G(d,p) basis sets. The absolute ^{13}C NMR shieldings for all carbons of **1**, **5** and **6** vary usually by <1 ppm, except C2 in **6**, which varies by <3 ppm.

The MP2/6–31G(d,p) geometries of the carbocations **1–6** (Table 1) reveal the structural consequences of the π-conjugative and σ-hyperconjugative stabilization of the positive charge.

In all structures **1–6** the central carbons C1, C2, C3 and C4 of the dienyl cation unit are coplanar. The C3—hydrogen and the C4—R (R = H, CH_3) substituents are approximately in the same C1—C2—C3—C4 plane (Plate 1).

This planar conformation provides maximum π-resonance stabilization by overlap of the vacant C2($2p^z$) orbital and the C3($2p^z$)—C4($2p^z$) π-bond which are both perpendicular to the C1—C2—C3—C4 plane. This allylic-type resonance (**IIa** ↔ **IIb**) leads to equalization of the C2—C3 and C3—C4 bond lengths in **1–6**: {av. $r_{(C2—C3)}$ and $r_{(C3—C4)}$ for **1–6**: 1.38 ± 0.03 Å; cf. parent allyl cation $r_{(C—C)}$ = 1.38 Å, [MP2/6–31G(d,p)]}. The additional hyperconjugative stabilization of the positive charge in **1–6** by interaction of the electron deficient $2p^z$-orbitals at C2 and C4 with the β-σ bonds of substituents at C1 and C4, respectively, changes the relative contributions of the resonance structures **IIa** ↔ **IIb**. In **3** the C3—C4 bond is noticeable longer ($r = 0.05$ Å) than the C2—C3 bond. The allenylmethyl cation resonance structure (**IIb**) contributes more than the vinyl cation resonance structure **IIa** because of additional stabilization of the positive charge at C4 by hyperconjugative overlap of the C4($2p^z$)-orbital with β–σ-C—H bonds of the C4—methyl groups. The bond length equalization effect gradually changes according to the substitution pattern monitoring the balancing of



Scheme 1. Buta-1,3-dienyl cations **1–6**

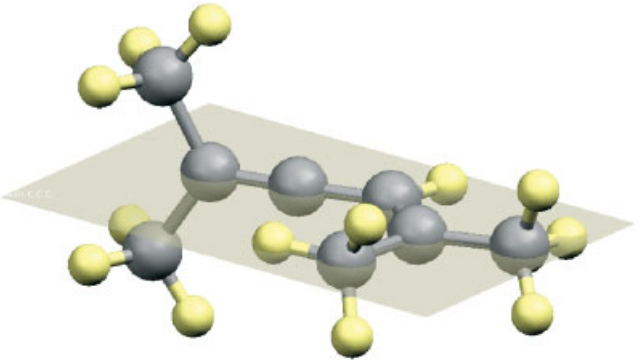
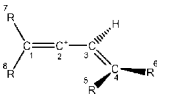


Plate 1. Structure of cation **5** (MP2/6–31G(d,p) geometry) showing the C1—C2—C3—C4 backbone plane

Table 1. Calculated C—C bond lengths (in Å) of carbocations **1**–**6** optimized at MP2/6–31G(d,p) level[a]



	C1—C2	C2—C3	C3—C4	C4—C5	C4—C6	C1—C7	C1—C8	C7—C8
1	1.292	1.362	1.389	1.468				
2	1.292	1.362	1.385		1.466			
3	1.295	1.354	1.402	1.480	1.480			
4	1.297	1.356	1.399	1.481	1.481		1.512	
5	1.297	1.359	1.397	1.483	1.482	1.515	1.515	
6	1.255	1.375	1.382	1.488	1.487	1.522	1.522	1.473

[a] For easy comparison a unified non-standard numbering scheme is used for the carbon atoms in **1**–**6**.

competing π-conjugative charge delocalization and σ-hyperconjugative stabilization of the positive charge by the substituents at C4 and C1 [($\Delta r_{(C3—C4/C2—C3)}$ (Å) = 0.048 (**3**); 0.043 (**4**); 0.039 (**5**); 0.027 (**1**); 0.023 (**2**)]. The allylic bonds C3—C4 (1.382 Å) and C2—C3 (1.375 Å) of the β-cyclopropylidene substituted vinyl cation **6** are essentially equidistant, indicating equal contributions of the limiting resonance structures **IIa** and **IIb** and thus comparable stability of the sp^2-hybridized tertiary carbocation structure of type **6b** and the sp-hybridized cyclopropylidene substituted vinyl cation structure of type **6a**.

The hyperconjugative interactions of the C4—methyl C—H σ-bonds are reflected by the different bond lengths of the three C—H bonds. Two C—H bonds with small torsion angles relative to the formally vacant p-orbital at C4 (which is perpendicular to the C1—C2—C3—C4 plane) are reasonably aligned for β–σ hyperconjugative overlap with the C4($2p^z$) orbital thus are elongated (1.095 Å, 1.091 Å) compared with the in-plane C—H bonds (1.084–1.086 Å) which do not hyperconjugate. As expected the β–σ-C—H hyperconjugation leads to shortening of the C4—CH_3 bond [r (Å) = 1.483 (**5**);1.480 (**3**); 1.481 (**4**); 1.466 (**2**); 1.468 (**1**); 1.487 (**6**), cf. propene sp^2-C—CH_3 bond, r = 1.50 Å (MP2/6–31G(d,p)].

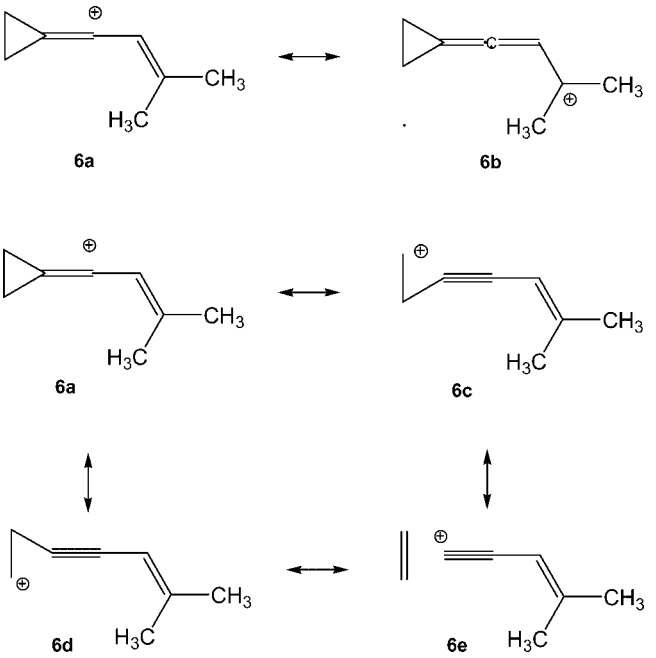
Substituents at carbon C1 are sterically fixed perpendicular to the C1—C2—C3—C4 plane, thus in plane with the formally vacant $2p^z$ orbital at the vinyl cation carbon C2 and therefore ideally arranged for β-C—C hyperconjugative interaction across the vinyl cation C1—C2 double bond. This leads to elongation of the C1—CH_3 σ-bonds in **4** and **5** [r = 1.52 Å, cf. propene sp^2-C—CH_3 bond, r = 1.50 Å (MP2/6–31G(d,p)].

In **6** the positive charge at C2 is stabilized in addition to the allyl resonance **6a** ↔ **6b** by hyperconjugative interaction between the antisymmetric Walsh orbital of the cyclopropylidene substituent and the formally empty $2p^z$-orbital at C2. In valence bond theory hyperconjugation of the cyclopropylidene substituent in **6** is described by contribution of 'no-bond' resonance limiting structures, the homopropargyl resonance structures **6c** and **6d** and the Dewar-type resonance structure **6e** (Scheme 2).

The hyperconjugative interaction of the cyclopropyl ring leads to elongation of the lateral C—C bonds [r = 1.52 Å, cf. cyclopropane 1.50 Å (MP2/6–31G(d,p)]. The basal C—C bond is shortened (r = 1.47 Å) because hyperconjugative stabilization of the positive charge reduces the electron density in the cyclopropyl ring and thus the antibonding character of the basal C—C bond. The vinyl cation C1—C2 double bond in **6** is significantly shortened (**6**, $r_{(C1—C2)}$ = 1.26 Å; cf. **3**, $r_{(C1—C2)}$ = 1.30 Å).

Chemical shifts

Quantum chemical calculations of ^{13}C NMR shieldings were performed using the GIAO-HF-SCF method,[40] the



Scheme 2. Conjugative and hyperconjugative resonance structures of cation **6**

GIAO-DFT-hybrid[41] method with the B3LYP functional and the GIAO-MP2 approach and different basis sets. The influence of geometry on the calculated chemical shifts has been explored for **1**, **5** and **6** by GIAO-MP2 NMR chemical shift calculations for structures optimized with different methods and basis sets (see above). The results indicated that MP2/6–31G(d,p) geometries are sufficiently accurate for the comparative study of cations **1**–**6**.

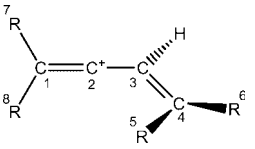
The influence of the basis set used for the NMR calculation was also investigated. In accord with earlier results[28,29] a polarized triple zeta basis (tzp)[39] for carbon atoms was found to be essential for the accurate determination of ^{13}C chemical shifts. In earlier ^{13}C NMR chemical shift calculations, which included highly correlated coupled–cluster methods, we used the more economical dz basis for hydrogen atoms. GIAO-MP2 NMR calculations for cations **1**–**6** with tzp basis at all atoms (MP2/tzp) compared with calculations with tzp basis at carbon and dz basis at hydrogen (MP2/tzp/dz) showed about 3 ppm smaller deviations for the MP2/tzp calculated data to the experimentally observed chemical shifts.

The overall best agreement between experimentally observed and calculated NMR chemical shifts for **1**–**6**, within the methods and basis sets used in this study, were obtained with GIAO-MP2/tzp NMR calculations for MP2/6–31G(d,p) optimized geometries. The relative chemical shifts (absolute shielding TMS; T_d symmetry, geometry optimized at MP2/6–31G(d,p) = 198.19 (GIAO-MP2/tzp); 185.59 (GIAO-B3LYP/tzp); 192.24 (GIAO-HF/tzp) are given in Table 2.

A comparison of chemical shifts calculated for the MP2/6–31G(d,p) optimized structures of cations **1**–**6** with different methods is illuminating.

Large deviations between GIAO-HF-SCF calculated and experimentally observed chemical shifts demonstrate that electron correlation effects on chemical shifts are very important for carbocation structures such as **1**–**6**.

Table 2. Calculated [a] and experimentally measured ^{13}C chemical shifts δ (ppm, vs TMS[b]) for carbocations **1**–**6**[d]



		C1	C2	C3	C4	C5	C6	C7	C8
1	exp.[15]	78.70	251.20	115.63	238.08	30.60			
	MP2	79.4	252.9	117.9	241.0	32.8			
	DFT	86.0	271.2	119.5	249.3	36.1			
	HF	88.4	293.4	107.8	252.5	27.5			
2	exp.[15]	74.91	256.30	117.90	239.80		32.83		
	MP2	75.6	258.9	120.4	243.7		35.2		
	DFT	82.0	277.1	121.9	251.5		38.7		
	HF	85.3	299.1	110.9	255.3		29.6		
3	exp.[c]	79.01	241.88	113.68	261.58	32.81	36.91		
	MP2	79.9	245.8	117.1	266.6	34.9	39.5		
	DFT	86.2	263.7	118.4	271.5	35.8	41.0		
	HF	89.0	280.7	106.5	276.4	30.1	34.1		
4	exp.[c]	90.34	243.97	114.43	259.16	32.64	36.63	9.46	
	MP2	93.2	245.8	117.5	261.7	33.9	38.5	11.9	
	DFT	102.0	267.5	118.7	266.3	34.6	39.7	12.4	
	HF	102.7	286.2	106.1	271.2	29.3	33.2	9.0	
5	exp.[c]	101.55	245.39	113.97	257.64	32.43	36.44	16.29	16.29
	MP2	105.2	244.0	116.8	257.6	33.1	37.6	18.4	18.7
	DFT	115.9	268.9	117.7	262.0	33.5	38.6	19.1	19.3
	HF	115.2	289.3	105.0	266.9	28.6	32.4	14.5	14.7
6	exp.[8]	63.66	202.66	111.72	228.92	27.18	30.62	39.63	39.63
	MP2	62.3	190.8	115.8	234.3	30.3	34.5	46.1	46.2
	DFT	73.2	218.4	117.9	246.4	31.5	36.2	45.2	45.2
	HF	66.1	239.6	106.0	249.7	26.8	30.3	29.9	30.1

[a] ^{13}C NMR chemical shifts were calculated for MP2/6–31G(d,p) optimized geometries, using the GIAO approach at the HF, DFT (B3LYP) and MP2 level and a tzp basis set for all atoms.

[b] Chemical shifts calculated relative to absolute shielding of TMS = 198.19 (GIAO-MP2/tzp); 185.59 (GIAO-B3LYP/tzp); 192.24 (GIAO-HF/tzp), T_d symmetry, geometry optimized at MP2/6–31G(d,p).

[c] In Ref. 6 we reported for cation **3**; **4** and **5** some early quantum chemical calculations on structure and charge with the STO-3G basis set using the Gaussian 76 program package.

[d] For easy comparison a unified non-standard numbering scheme is used for the carbon atoms in **1**–**6**.

The chemical shift for carbon C2 and C4 of the allyl cation resonance system is calculated as being much too deshielded with the HF-SCF method. The deviation for the vinyl cation carbon C2 is between 44 ppm in **5** and 37 ppm in **6** (HF/tzp). C4 is calculated as being too deshielded between 21 ppm in **6** and 9 ppm in **5**. These data support the earlier conclusions,[13,28,29] that the correlation error (i.e. the difference between the HF-SCF and MP2 chemical shifts) is very large for the sp-hybridized carbon of a vinyl cation.

As a consequence of the large correlation error the HF-SCF/tzp calculated NMR chemical shifts for cations **3**, **4** and **5** predict a reverse relative assignment of the terminal carbons C2/C4 of the allyl resonance structural unit [δ(C2/C4), **3** Exp.: 241.88/261.58. Calc: 280.73/276.37. **4** Exp.: 243.97/259.16. Calc: 286.20/271.18. **5** Exp.: 245.39/257.64. Calc: 289.33/266.89]. For **1**–**5**, the shift for C1, the sp^2-hybridized β-carbon of the vinyl cation, is calculated to be about 14–9 ppm too deshielded (HF/tzp). The chemical shift for the central sp^2-hybridized carbon C3 of the allyl subunit is calculated to be about 9–6 ppm too shielded for all cations **1**–**6** (HF/tzp). For cation **5** a reverse assignment for the signals of C1 and C3 is calculated [Δ (C1/C3), Exp.: 101.55/113.97. Calc: 115.23/105.01]. This shows that the HF-SCF method does not provide an adequate treatment of the electronic effects responsible for the chemical shift in these types of carbocations.

The GIAO-DFT approach has evolved as a standard tool in the calculation of NMR chemical shifts, because of reasonable accuracy and cost efficiency. DFT methods lack, however, possibilities for systematic improvements compared with traditional methods for treating electron correlation. The DFT calculated NMR chemical shifts (B3LYP/tzp//MP2/6–31G(d,p)) for carbocations **1**–**6** show deviations (deshielding) from the experimental values, which are smaller than with the basic HF-SCF approach but still very significant. The deviations are: 23–15 ppm for the vinyl cation carbon C2, 17–10 ppm for the allylic carbon C4 (but 4 ppm for **5**) and 14–10 ppm for the β-carbon C1. For cations **5** and **6** some deviations calculated with the B3LYP/tzp method are even larger than those calculated at HF/tzp. The B3LYP/tzp calculated shift for the central allyl carbon C3 in **1**–**6** deviates by 6–4 ppm.

The B3LYP/tzp calculated chemical shifts predict the wrong order for the shift of the carbons C2/C4 in cation structures **4** [δ(C2/C4), Exp.: 243.97/259.16. Calc: 267.50/266.32] and **5** [δ(C2/C4), Exp: 245.39/257.64. Calc: 268.95/261.96]. It is known that GIAO-DFT methods, owing to an overestimation of the paramagnetic contribution to the chemical shift, predict overly deshielded chemical shifts.[42] The non-systematic deviations obtained for the B3LYP calculated chemical shifts in the resonance delocalized allyl-type cations **1**–**6** prevent reliable extrapolation schemes and scaling methods, such as have been used for simple alkyl cations.[43]

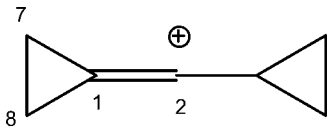
The results show that the chemical shifts predicted by GIAO-HF-SCF and GIAO-DFT calculations cannot be relied upon for unequivocal assignment of NMR signals in these types of dienyl cations.

The second-order Møller–Plesset perturbation theory approach for taking into account electron correlation in chemical shift calculations (the GIAO-MP2 method) was found to give much more reliable results. GIAO-MP2/tzp//MP2/6–31G(d,p) calculations for all structures **1**–**6** predicted the sequence of the signals in the ^{13}C NMR spectrum correctly (Table 2). In the methyl-substituted dienyl cations **1**–**5** the deviation of the calculated shift for the C2/C4 carbons from the experimentally observed shift is generally smaller than 5 ppm [$\Delta\delta$ $C2_{(calc-exp.)}$, $C4_{(calc-exp.)}$ (ppm): 1.7, 2.9 (**1**); 2.6, 3.9 (**2**), 3.9, 5.0 (**3**); 1.8, 2.5 (**4**); -1.4, -0.1 (**5**)]. The deviations for the other sp^2-hybridized carbons C1 and C3 for **1**–**5** are between 0.7 and 3.6 ppm. The calculated shifts for the methyl groups in **1**–**5** agree with experiment within 2.6 ppm. The mean deviation ($\approx$ 3–4 ppm) between experimental and GIAO-MP2/tzp calculated chemical shifts for all carbons in **1**–**5** is only somewhat larger than that reported for the GIAO-CCSD(T) calculations for **1** and **2** ($\approx$ 2 ppm).[15]

The GIAO-MP2/tzp approach is therefore a suitable method to describe the electronic properties of vinyl cations, which are simultaneously stabilized by π-resonance and σ-C—C hyperconjugation of β-methyl groups. The GIAO-MP2/tzp scheme for cations **1**–**5**, is only $\approx$ 2 ppm less accurate than coupled-cluster methods and is only a small fraction of the cost.

The MP2/tzp calculated ^{13}C NMR chemical shifts of the cyclopropylidene substituted dienyl cation **6** show for all but the C1 position larger deviations from the experimental shifts than the cations **1**–**5**. Provided that the MP2/6–31G(d,p) model used for the geometry optimization describes the geometrical distortions, accomplished by the hyperconjugative interactions of a cyclopropyl ring with a vacant p-orbital, with sufficient accuracy, as is generally assumed, it can be concluded that the GIAO-MP2/tzp approach overestimates the influence of σ-delocalization of the positive charge into the cyclopropane subunit on the chemical shifts. Carbon C2 is calculated as being 11.9 ppm too shielded, whereas C4 is calculated 5.4 ppm too deshielded. The difference between the HF-SCF and MP2 calculated chemical shifts is -49 ppm for C2 and -15 ppm for C4. The methylene groups of the cyclopropane ring that are more involved in hyperconjugative charge delocalization than the C4—CH_3 groups show a larger deviation from experiment (6–7 ppm deshielding) compared with the C4—CH_3 groups (3–4 ppm deshielding). Accordingly the electron correlation effect for the C7/C8—CH_2 groups (16 ppm) is much larger than for the C5/C6—CH_3 groups (3–4 ppm). It has been demonstrated that the correlation correction for the 1-cyclopropylcyclopropylidenemethyl cation **7** is too large to be described adequately by the GIAO-MP2 method and that higher orders of perturbation theory such as

coupled-cluster methods are required to rectify the problem.[28]



7

The correlation corrections for carbon C2 in **7** are 66 ppm shielding from HF to MP2 and 23 ppm deshielding from MP2 to CCSD(T). This is accompanied by a 16 ppm deshielding HF to MP2 correction and a shielding 4 ppm MP2 to CCSD(T) correlation correction for the shift of the cyclopropylidene methylene groups C7 and C8. These electron correlation corrections for **7** are in the same direction as for cation **6** calculated deviations of the MP2/tzp shifts from the experimentally measured chemical shifts for C2 and C7/C8. Therefore it can be anticipated that CCSD(T) calculations would give much closer agreement to the experimentally observed shifts for cation **6**.

Quantum chemical calculations were performed with the Turbomole program[44] on a Linux Athlon cluster assembled by Dr. Koch, Transtec AG, Tübingen, and the Gaussian 98 program[45] on SUN Ultrasparc and Linux Athlon cluster hardware.

CONCLUSION

A comparison of experimentally measured and calculated ^{13}C NMR chemical shifts for a closely related series of various substituted vinyl cations is presented. The MP2/6–31G(d,p) optimized structures support the interpretation of the experimental NMR data. The quantum chemically calculated structural data reveal the geometrical consequences of π-conjugation and σ-C—H and σ-C—C hyperconjugation and their interplay and dependence in a series of various substituted carbocations.

The calculations of ^{13}C NMR chemical shifts show large deviation between the HF-SCF calculated and the experimentally observed shifts, particular for the carbons bearing the positive charge (up to 44 ppm for C2 in **5**). GIAO-HF and likewise GIAO-DFT (B3LYP) calculations predict the wrong order of ^{13}C NMR signals in the low-field region of the spectra of cations **3** (GIAO-HF), **4** and **5**. At the GIAO-DFT (B3LYP) level the errors are smaller than with the GIAO-HF method, but still large (>23 ppm for C2 in **4**).

The second-order Møller–Plesset perturbation approach for electron correlation implemented in the GIAO-MP2 method with a tzp basis for all atoms gives the correct sequence of ^{13}C NMR signals and performs satisfactorily (mean deviation $\approx$ 3–4 ppm) for all carbons of cations **1–5**. Owing to the special hyperconjugative abilities of cyclopropyl substituents, GIAO-MP2/tzp calculations for cation **6** give some larger deviations ($\approx$ 6–9 ppm). The GIAO-MP2/tzp calculated NMR data strongly support the validity of all calculated structures **1–6** and the interpretation of the experimental results and allow conclusive and unequivocal assignment of the ^{13}C NMR signals.

Taking the data presented here for cation **6** and the earlier results for **7**,[28] it appears that coupled cluster methods, such as the GIAO-CCSD(T) approach, which minimize the electron correlation error, are required to achieve $\leq$ 3 ppm agreement with experiment for cyclopropyl substituted vinyl cations,[29] which exhibit some 'unusual' electron distribution due to the special electronic properties of the cyclopropane substituent.

In summary, we have found that GIAO-HF and GIAO-DFT calculations of chemical shifts for vinyl cations cannot be relied upon. The GIAO-MP2/tzp scheme, however, gives satisfactory results, except in special cases where electron correlation errors are large.

Supplementary material

Additional material is available in Wiley Interscience.

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