NMR Spectroscopic and quantum chemical characterization of the (*E*)- and (*Z*)- isomers of the penta-1,3-dienyl-2-cation[†]

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ABSTRACT: Dilute solutions of the (*E*)- and (*Z*)- isomers of pent-1,3-dienyl-2-cations (**1**) were obtained from reaction of 4-chloro-1,2-pentadiene (**2**) with SbF_5 in SO_2ClF/SO_2F_2 at $-135\,°C$ using high-vacuum co-condensation techniques. The experimental NMR spectra of the mixture of the two isomers were compared with quantum chemical ^{13}C NMR chemical shift calculations at HF-SCF, MP2, CCSD and CCSD(T) levels using MP2/tzp geometries. Quantum chemical shift calculations were performed with a tzp basis (9s5p1d/5s3p1d) for carbon and a dz basis (4s/2s) for hydrogen using gauge-including atomic orbitals (GIAOs). The HF-SCF calculations deviate significantly for the positively charged carbon atoms of the allyl-type resonance system showing up to 40 ppm too deshielded values compared with the experimentally observed chemical shifts. The HF-SCF approach is therefore not sufficient in predicting satisfactorily the shielding tensors in this type of carbocation. Inclusion of electron correlation, however, allows an unequivocal assignment of the spectra of the *Z*- and *E*-isomers. The mean deviation between experimental and calculated NMR chemical shifts at the CCSD(T) level is 1.8 and 2.0 ppm for (*Z*)- and (*E*)-**1**, respectively. The dienyl cations (*E/Z*)-**1** are the smallest vinyl cations ever generated as persistent species in superacidic solutions and observed by ^{13}C NMR spectroscopy. These carbocations were structurally fully characterized by advanced *ab initio* quantum chemical calculations of structure and NMR chemical shifts. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: carbocations; vinyl cations; NMR spectroscopy; quantum chemical calculations; coupled-cluster NMR chemical shift calculations
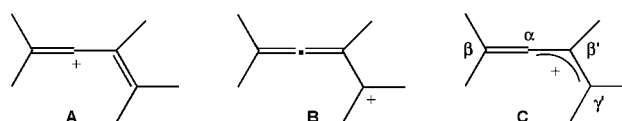
INTRODUCTION

The interplay between theory and experiment is especially successful in the field of reactive intermediates. The accurate prediction of the spectroscopic properties of short-lived molecules by modern quantum chemistry facilitate their experimental characterization and identification. The combined *ab initio*–IGLO (or GIAO)–NMR approach has proven to be more than only a substitute for unavailable x-ray structures in carbocation chemistry.[1,2]

However, the disregard or the non-biased treatment of electron correlation in *ab initio* NMR chemical shift calculations leads in difficult cases to unsatisfactory or even erroneous results. Prominent examples, where theoretical methods for the *ab initio* calculation of

NMR chemical shieldings based on Hartree–Fock theory fail, are, among others,[3] unsaturated carbocations such as allyl[4] and vinyl cations.[5] We will show in this paper that also for another family of unsaturated carbocations, the dienyl cations, the combined *ab initio*–GIAO–NMR approach leads to very good agreement with experiment, provided that electron correlation is adequately included.

Stabilized vinyl cations have recently become available as long-lived species in solution and have been studied by ^{13}C NMR spectroscopy.[6] Vinyl-substituted vinyl cations (dienyl cations) are efficiently stabilized by π-conjugation. A dienyl cation **C** is best described as a resonance hybrid between an α-vinylvinyl cation (1,3-dien-2-yl cation, **A**) and an allenylmethyl cation (1,2-butadien-4-yl cation, **B**) (Scheme 1).

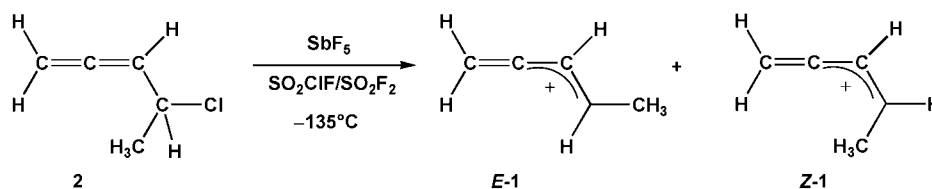Substituted dienyl cations are formed in the course of solvolysis reactions as short-lived intermediates by

Scheme 1

Scheme 2

ionization of methyl-substituted 2-bromo-1,3-buta-dienes.[7] The acid-catalyzed hydrolysis of α-allenyl alcohols proceeds via dienyl cation intermediates to give α,β-unsaturated ketones.[8] Using superacids, appropriate experimental methods and suitable progenitors, this reaction can be terminated at the carbocation stage. Reaction of methyl substituted tertiary α-allenyl alcohols with SbF$_5$ in non-nucleophilic solvents at low temperatures leads to formation of corresponding persistent dienyl cations in solution.[9]

RESULTS AND DISCUSSION

The electron distribution in dienyl cations is sensitive to the substitution pattern at the terminal C-atoms C-β and C-γ′. Decreasing substitution at C-γ′ should be accompanied by charge transfer to C-α. Thus, the contribution of the vinyl cation resonance structure should be enforced by decreasing substitution at C-γ′. Following this lead, we prepared stable ion solutions of secondary dienyl cations. Using advanced co-condensation techniques, dilute solutions of the E- and Z-isomers of pent-1,3-dienyl-2-cations (**1**) were obtained from reaction of the secondary allenylethyl chloride **2** with SbF$_5$ in SO$_2$ClF/SO$_2$F$_2$ at −135 °C (Scheme 2).[10,11]

Two sets of five signals were observed in the ^{13}C NMR spectra (see Fig. 1 and Table 1). Each set corresponds to one stereoisomer **E-** or **Z-1**, respectively [for convenience these notations are used for (E)-**1** and (Z)-**1**].

The intensity ratio between each pair of signals is 1:1.4, indicating a predominance of one isomer. The two isomers **E-** and **Z-1** do not interconvert up to −90 °C, when the cation decomposes rapidly. In qualitative agreement, quantum chemical calculations (MP2/tzp) of the perpendicular conformer of **1** (point group = C_1), which is the transition state for the interconversion of the

(E)- and (Z)-isomers, predict a high barrier of 23 kcal mol^{-1} for the (E/Z) isomerisation. The assignment of the ^{13}C NMR signals of (**E**)- and (**Z**)-1 were made using ^{1}H-coupled ^{13}C NMR spectra.

The occurrence of the allyl-type resonance in **1** is shown by the highly deshielded C-α [251.20 ppm (**Z-1**) and 256.30 ppm (**E-1**)] and C-γ′ [238.08 ppm (**Z-1**) and 239.80 ppm (**E-1**)]. The unusual high-field resonance for olefinic C-β [78.70 ppm (**Z-1**), 74.91 (**E-1**)] is characteristic for a vinyl cation[12] and is due to the shielding influence of the neighboring sp-hybridized C-α. Also, the central methine carbon C-β′ appears at much higher field than in ordinary allyl cations for example, the chemical shift of the central carbon in (E,E)-1,3-dimethylallyl-cation is 148.3 ppm.[13] The five carbon atoms containing cations **Z/E-1** are so far the smallest vinyl cations characterized by NMR spectroscopy in solution.

C-α in **Z-1** is deshielded by 8.7 ppm compared with the tertiary dienyl cation **3** (see Table 1), while the ^{13}C NMR signal of C-γ′ is shifted to higher field by 24.0 ppm. This strongly supports the hypothesis that decreasing substitution at C-γ′ will enforce the vinyl cation canonic structure **A** on the expense of the resonance structure **B**.

For the further structural characterization of the dienyl cations **E/Z-1**[14] we performed quantum chemical *ab initio* calculations. The structures of **E/Z-1** were calculated at the second-order Møller–Plesset perturbation theory level[15] using a polarized triple-zeta (tzp) basis.[16] ^{13}C NMR chemical shifts were computed using the Hartree–Fock self-consistent-field (HF-SCF) ansatz and various electron-correlated approaches ranging from MP2 up to those based on the coupled-cluster (CC) ansatz.[17] To ensure gauge-origin independence, these calculations were performed using gauge-including
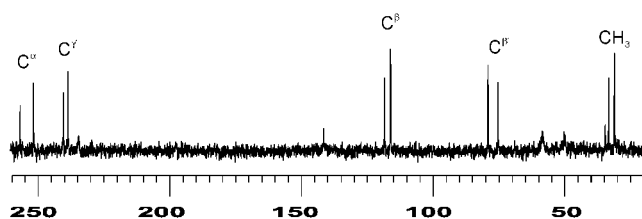

Figure 1. 100.62 MHz ^{13}C NMR spectrum of (**E**)-/(**Z**)-1 in SO$_2$ClF/SO$_2$F$_2$ (3:2) at −120 °C; Ref. δ (CD$_2$Cl$_2$) = 52.8 ppm

Table 1. ^{13}C NMR parameters for **E/Z-1** in SO$_2$ClF/SO$_2$F$_2$ at −120 °C [chemical shifts in ppm vs external CD$_2$Cl$_2$, δ (CD$_2$Cl$_2$) = 52.8 ppm; in parentheses, $^1J_{CH}$ coupling constants in Hz][a]

	Cα	Cβ	Cβ′	Cγ′	CH$_3$
Z-1	251.20	78.70	115.63	238.08	30.60
		(175)	(185.3)	(170)	(130)
E-1	256.30	74.91	117.90	239.80	32.83
		(175)	(185.5)		(130)
3	242.50	79.40	114.70	262.10	33.22, 37.22

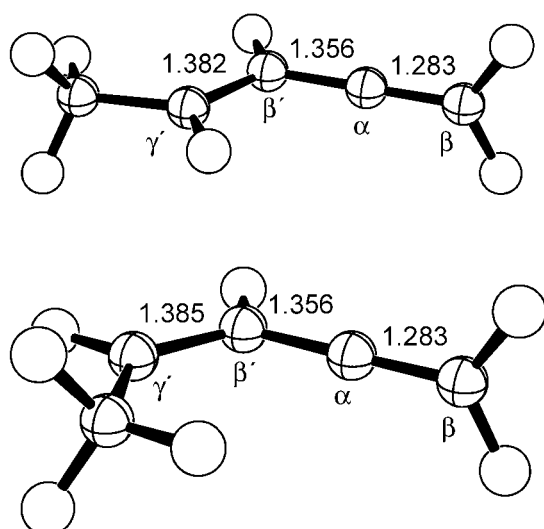[a] For comparison, the chemical shifts of the 2-methylpenta-1,3-dienyl-2-cation **3** are given.[9a]

Figure 2. Calculated MP2/+zp-geometry for (*E*)- and (*Z*)-isomers of the penta-1,3-dienyl-2-cation (bond lengths in Å)

atomic orbitals (GIAOs).[18] As in previous work,[4,5] the NMR chemical shift calculations were carried out with a tzp basis at C and a double-zeta (dz) basis at H.[16] The optimized structures reveal the structural consequences of the π-conjugation (Fig. 2).

The minimum conformations of **E-1** and **Z-1** provide maximum overlap between the empty C(2p) orbital at C-α and the π-bond between C-β' and C-γ'. The importance of allylic-type resonance (**1A** $\leftrightarrow$ **1B**), is reflected in the equidistant C_{α}—$C_{\beta'}$ (1.356 Å for both isomers) and $C_{\beta'}$—$C_{\gamma'}$ (1.382 Å for **E-1** and 1.385 Å for **Z-1**) bonds lengths (see Fig. 2), reminiscent of the allyl cation [r(C—C) = 1.378 Å, MP2/tzp]. The vinylic C_{β}=C^+ double bond length is calculated to be 1.283 Å

for both **E**- and **Z-1** and thus is intermediate between those in acetylene (1.211 Å, MP2/tzp) and ethene (1.331 Å, MP2/tzp).

Quantum chemical ^{13}C NMR chemical shift calculations using various orders of Møller–Plesset perturbation theory (MP2, MP3, MP4)[19] and CC schemes such as the CC singles and doubles (CCSD) and the CCSD approach augmented by a perturbative treatment of triple excitations[20,21,22] were successfully used to establish in the past the validity of theoretically determined geometries for carbocations.[3] The NMR chemical shift of **E/Z-1** (versus TMS; MP2/tzp, T_d symmetry) were calculated at the HF-SCF, MP2, CCSD and CCSD(T) levels using the geometries obtained at the MP2/tzp level and the results are summarized in Table 2.

The large deviation between HF-SCF-calculated and experimentally observed chemical shifts for C-α (38.5 and 41.3 ppm too deshielded in **Z**- and **E-1**, respectively) and to smaller extent of C-γ' (10.8 and 11.9 ppm in **Z**- and **E-1**) clearly point to the deficiencies of the HF-SCF-approach in predicting the shielding tensors of the positively charged carbon atoms C-α and C-γ'. The basic HF-SCF treatment does not provide an adequate treatment whereas inclusion of electron correlation even the modest MP2 level improves the situation dramatically (Fig. 3).

The electron correlation correction (i.e. the difference between the HF-SCF and MP2 chemical shifts) for the
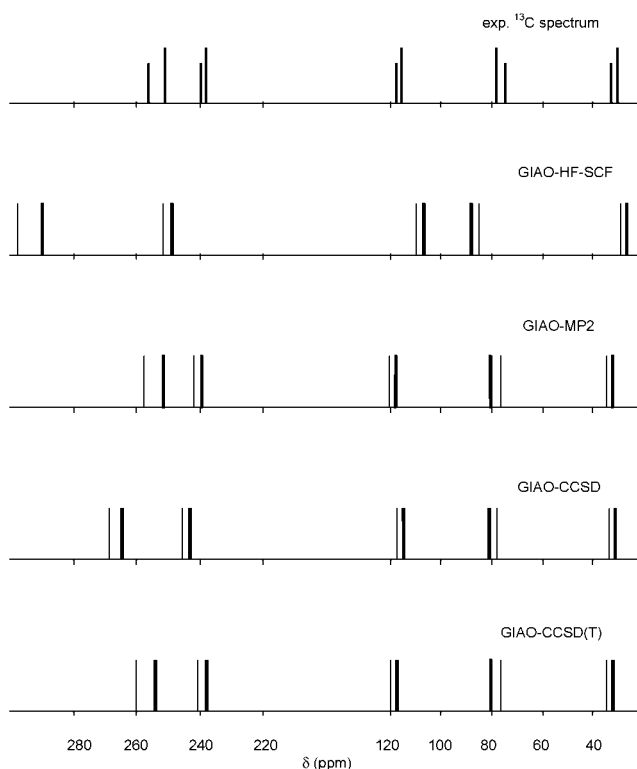
Table 2. Calculated ^{13}C NMR chemical shifts δ for (**E**)/(**Z**)-1 (in ppm vs TMS[a]) using different quantum chemical methods[b] and MP2/tzp optimized geometries

	HF-SCF	MP2	CCSD	CCSD(T)
(**Z**)-1				
Cα	289.7	251.6	264.6	254.1
Cβ	88.2	80.3	81.2	80.3
Cβ'	106.8	117.8	114.6	117.4
Cγ'	248.9	239.3	243.3	238.0
CH$_3$	26.9	32.5	31.4	32.3
(**E**)-1				
Cα	297.6	257.6	268.7	260.1
Cβ	85.0	76.5	77.8	76.7
Cβ'	109.8	120.2	117.3	119.6
Cγ'	251.7	242.1	245.6	240.6
CH$_3$	29.0	34.9	33.8	34.5

[a] Chemical shifts were first obtained with respect to methane and then converted to the usual TMS scale using $\delta(CH_4) = -1.348$ in the case of HF-SCF and -3.898 for all other methods. For further details, see Ref. 5.
[b] Chemical shift calculations were performed with a tzp basis (9s5p1d/5s3p1d) for carbon and a dz basis (4s/2s) for hydrogen[16] using gauge-including atomic orbitals (GIAOs).

Figure 3. Comparison of experimental and calculated ^{13}C NMR chemical shifts for (**E**)-/(**Z**)-1 (calculated shifts for (**Z**)-1 are shown in bold)

positively charged C-atoms is large (-37.2, -9.6 and -40.0 ppm, -9.6 ppm for C-α and C-γ' in **E/Z-1**, respectively). At the CCSD(T) level all of the calculated ^{13}C NMR shifts differ by not more than 3.9 ppm from the experimental results. The mean deviation between experimental and calculated NMR chemical shifts at the CCSD(T) level is 1.8 and 2.0 ppm for **Z-** and **E-1**, respectively. It is noteworthy, but most likely fortuitous, that the lower level MP2 calculation gives marginally better results.

The high-level CC chemical shift calculations allow an unequivocal assignment of **Z-1** and **E-1** (see Fig. 3) According to the calculations the predominately formed isomer is **Z-1**. The computed energy difference between the isomers **E-1** (point group C_S) and **Z-1** (point group C_S) amounts to 1.8 kcal mol^{-1} (MP2/tzp) in favor of **E-1**, hence the predominant formation of **Z-1** is not thermodynamically controlled. The assignment of the [13]NMR spectrum is in line with empirical chemical shift arguments: (1) owing to steric interaction the olefinic carbons in 1,2-disubstituted alkenes are generally more shielded in the Z-isomer than in the E-isomer; (2) the signal for the methyl group attached to the double bond in a 1,2-disubstituted alkene is more shielded in the Z-isomer than in the E-isomer. Both chemical shifts arguments applied to **1** indicate that **Z-1** is the predominant isomer in the experimentally investigated sample (the more intense signals for C-γ', C-β' and the methyl carbon are at higher field).

The pent-1,3-dienyl-2-cations **E/Z-1** are the smallest vinyl cations ever observed as persistent species in superacidic solutions. They were structurally fully characterized by advanced *ab initio* quantum chemical calculations of structure and NMR chemical shifts.

EXPERIMENTAL

4-Chloro-1,2-pentadiene **2**.[10,23] A suspension of 1.8 g of triphenylphosphane in 30 ml of CFCl$_3$ was cooled to $-90\,°C$. At this temperature a solution of 1.82 ml of hexachloroacetone in 5 ml of CFCl$_3$ was added. To the resulting white slurry a solution of 3,4-pentadien-2-ol[24] in 10 ml of CFCl$_3$ was added dropwise. The temperature of the reaction mixture was held at $-90\,°C$ for one hour, then all volatiles were distilled off *in vacuo* and collected in a cooling trap, held at the temperature of liquid nitrogen. CFCl$_3$ was removed by distillation and the residue was fractionated under reduced pressure. Yield: 380 mg of **2** (63%). ^{13}C NMR (63 MHz, δ [13]C$_{CDCl_3}$ 77.0), δ 207.44 (m, central allenic), 95.21 (dm, $^1J_{CH} = 168.79$ Hz, terminal allenic CH), 78.27 (td, $^1J_{CH} = 168.3$ Hz, $^3J_{CH} = 7.1$ Hz, terminal allenic CH$_2$) 54.88 (dm, $^1J_{CH} = 150$ Hz, CH), 24.81 (q, $^1J_{CH} = 129.1$ Hz, CH$_3$). ^{1}H NMR (250 MHz, δ [1]H$_{CDCl_3}$ 7.24), δ 5.40 (m, 1H), 5.0–4.85 (m, 2H), 4.65–4.50 (m, 1H), 1.59 (d, $^3J_{HH} = 6.7$ Hz, 3H).

The general experimental technique and the special apparatus for the generation of carbocations have been described.[10] At a pressure of 8×10^{-6} mbar, 0.3 mmol of **2** dissolved in 0.9 ml of SO$_2$ClF and 0.5 ml (6.9 mmol) of SbF$_5$ was distilled synchronously through seperate nozzles on to a homogenous matrix of 1.2 ml of SO$_2$F$_2$ and 1.7 ml of SO$_2$ClF cooled to $-196\,°C$. An orange solution of **E/Z-1** was obtained by warming to -140 to $-130\,°C$. The solution was transferred under high vacuum at $-135\,°C$ into 10 mm NMR tubes, which were then sealed under vacuum and stored at $-196\,°C$.

^{1}H NMR and ^{13}C NMR spectra of the carbocation solutions were measured on a Bruker 400 NMR spectrometer equipped with a variable-frequency fluorine lock channel and a 10 mm ^{13}C/^{1}H/^{19}F/^{2}H probe, using the fluorine resonance of SO$_2$ClF or SO$_2$F$_2$ as an internal lock. The probe temperature was calibrated with a ^{13}C chemical shift thermometer using neat 2-chlorobutane[25] in a capillary in an NMR tube filled with SO$_2$ClF admixed with other solvents.

All quantum chemical calculations were performed using a local version of the ACES II program package.[26] All calculations were performed with all electrons correlated and Cartesian polarization functions.

Acknowledgements

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