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Equilibrating system of 2-methylbenzonorbornen-2-yl type cations

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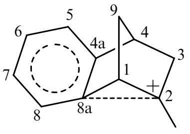
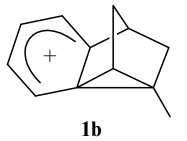
The nature of the changes in the ^{13}C NMR spectra of the 2-methylbenzonorbornen-2-yl carbocation caused by the substitution of deuterium for hydrogen in the methyl group and by temperature variation suggests that in fact this cation represents a system of two or more species with differing extents of π-bridging separated by a very low energy barrier.

One of the intriguing questions of carbocation chemistry is connected with the existence of one or more minima on the potential energy surface (PES) of carbocation systems with structures which allow nonclassical effects. A particular case of such effects, π-bridging, is characteristic of the tertiary 2-benzonorbornenyl cations.[1–3]

Previously, on the basis of NMR data, static nonclassical structures of type **1a**, having the sole minimum on the PES, have been proposed for the 2-methylbenzonorbornen-2-yl carbocation $C_{12}H_{13}{}^+$ **1**[1,2] and for a number of its analogues[4,5] generated under long-life conditions.[†] However, data recently obtained[6] using the method of isotopic perturbation for the long-lived 2,3,3-trimethylbenzonorbornen-2-yl carbocation $C_{14}H_{17}{}^+$ **2** have shown that this cation may represent a dynamic system of two ions differing in their degree of π-bridging.



1a



1b

The present work deals with the question of whether there is one or more minima on the PES of ion **1**, the parent cation of the series of tertiary 2-benzonorbornenyl cations.

In contrast to the ^{1}H NMR spectrum of cation **1**, the temperature independence of which allows the conclusion[1] that this cation is a static one **1a**, the ^{13}C NMR spectra of 2-*exo*-chloro-2-methylbenzonorbornene **3** in FSO_3H/SbF_5–SO_2ClF, where the same ion should be formed, shows a distinct dependence of carbon chemical shifts on temperature (Table 1). The opposing directions of the shifts for some atoms (for example, C^2 *vs.* C^1, C^{8a} *vs.* C^{4a}) with a variation in temperature excludes the possibility of all the changes of chemical shifts being attributable to the variability of the

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[†] The authors of ref. 1 seem not to exclude the possible existence of an additional high-level minimum corresponding to the 2-methylbenzonortricyclyl cation **1b** of phenonium type.

Table 1 ^{13}C NMR data for the ion **1** and its deuterated analogue.

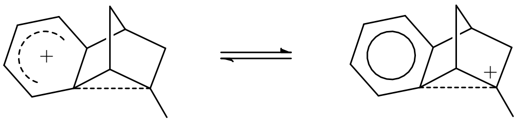
	Atom											
Parameter (T/°C)	C^1	C^2	C^3	C^4	C^{4a}	C^5	C^6	C^7	C^8	C^{8a}	C^9	C_{CH_3}
$\delta_H(-65)^a$	84.18	199.94	57.2	41.79	177.23	132.11	143.14	124.77	150.25	104.89	53.61	26.23
$\delta_D(-65)-\delta_H(-65)^b$	0.36	−3.16	0.13[c]	<0.1	0.61	<0.1	0.30	<0.1	0.55	−0.67	<0.1	[d]
$\delta_D(-122)-\delta_H(-122)^b$	0.33	−3.47	<0.2	<0.2	0.68	<0.2	0.32	<0.2	0.58	−0.73	<0.2	[d]
$\delta_H(-65)-\delta_H(-122)^e$	0.91	−4.47	0.41	0.17	0.95	0.34	0.79	0.14	0.69	−0.73	0.01	−0.32

[a] Chemical shifts of the ion **1** (ppm, internal standard CD_2Cl_2, δ 53.3 ppm). [b] Isotope shifts (ppm). When isotope shifts are not observed their upper limits are estimated. [c] The value may be of the opposite sign. [d] Signal of the CD_3 group is not observed. [e] Temperature effect on chemical shifts of the ion **1** (ppm), that of CD_2Cl_2 being taken as zero.

position of the internal standard signal (*cf.* ref. 7). It is noteworthy that the sensitivity of the atom C^2 chemical shift to temperature changes (from -0.053 ppm K^{-1} at -65 °C up to -0.101 ppm K^{-1} at -122 °C) far exceeds, in absolute magnitude, those of static carbocations[8] and neutral molecules containing no highly polarizable groups.[9] This suggests that on ionization of chloride **3** a rapidly equilibrating system of at least two cations (*cf.* ref. 10) is formed and not a static ion **1a**.

Data obtained by isotopic perturbation[11,12] for cation **1** support this assumption: substitution of the CH_3 group hydrogens by deuterium results in considerable isotope shifts not only for the carbocationic centre (C^2 atom), but also for a number of carbons three or more bonds from the site of deuterium insertion (Table 1, *cf.* refs. 13 and 14).

The observed magnitudes and signs of both temperature and isotope effects on chemical shifts indicate that the above, equilibrating, system may include two ions of a benzonorbornen-2-yl type, **1c** and **1d**, differing in the degree of π-bridging (Figure 1). The signs of the temperature effects on chemical shifts testify to the exothermicity of the process **1c**→**1d**.



1c **1d**

The energy barrier for the process **1c**⇄**1d** is very low, it cannot be 'frozen out' on the NMR time-scale even at −127 °C. One cannot even exclude the absence of an energy barrier. In this case the PES of the ion **1** represents a shallow well with a flat inclined bottom (Figure 2), a vibration with a large amplitude between the nuclear configurations **1c** and **1d** being analogous to the equilibrium between **1c** and **1d**.[‡]

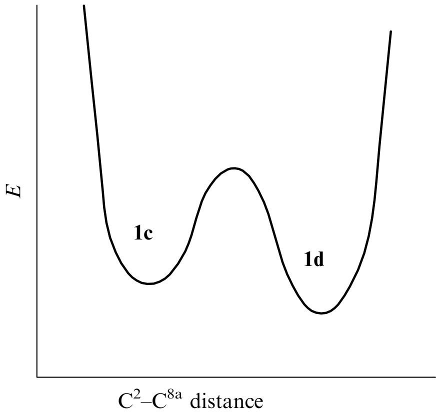


Figure 1

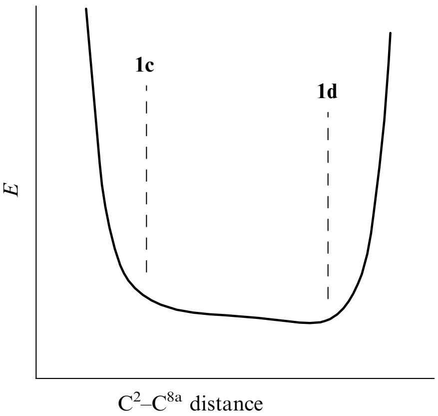


Figure 2

However, comparing data of the present study with that obtained earlier for a related carbocation system $C_{14}H_{17}^+$, **2**[6] does not suggest that the PES of the system $C_{12}H_{13}^+$ **1** has a single minimum. The value of the isotope effect on the C^2 chemical shift for the system **2** (-3.10 ppm at -100 °C) is virtually equal to that for the system **1**, while the temperature effect (-0.009 ppm K^{-1} at -100 °C) differs significantly. This can be easily explained in terms of the existence of two minima on the PES's of the carbocation systems **1** and **2** (Figure 1): the observed difference in the temperature effects for these systems may result from the unequal differences in the enthalpies of the equilibrating ion structures.

Quite the opposite situation arises in terms of Figure 2 where a possible manifestation of temperature effects owing to the existence of two minima is absent. The width of the potential well depicted in Figure 2 is rather large and, thus, excited vibration levels may be considerably populated even at low temperatures. In this case, the temperature and isotope effects observed for each system (**1** and **2**) would be explicable provided that the potential energy wells are unsymmetric.[10] However, it is hardly possible to imagine any differences between these wells which could be responsible for the nearly equal isotope effects and dissimilar temperature effects observed for the closely related systems **1** and **2**.

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[‡] This is precisely the interpretation which was given earlier to account for the data obtained on the temperature variation and isotope perturbation for 2-methylnorborn-2-yl and 2-methylbicyclo[2.2.2]oct-2-yl cations.[10]

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