Large N.M.R. Isotope Shifts for the ^{13}C Resonance at the Cation Centre of the 2-Methyl-2-norbornyl Cation

David A. Forsyth* **and Chitchanun Panyachotipun**

Department of Chemistry, Northeastern University, Boston, Massachusetts, MA 02115, U.S.A.

N.m.r. signals for the cationic centre of all of the ten possible singly deuteriated positional isotopomers of 2-methyl-2-norbornyl cation have been observed with chemical shifts varying by 3 p.p.m.

We have previously reported that unusually large (>1 p.p.m.) upfield n.m.r. isotope shifts are associated with deuterium labelling of the 3-position of methyl group of the 2-methyl-2-norbornyl cation (**1**).[1—3] Now it is evident as shown in Figure 1 that each of the ten ring-deuteriated positional isotopomers of (**1**) has a different chemical shift for the cation centre. The chemical shifts vary by 3 p.p.m. depending upon the location of a single deuterium. Particularly noteworthy is that deuterium substitution at the 6-*exo* position induces an unusually large downfield shift in the ^{13}C resonance of the cation centre.

Solutions of (**1**) were prepared from variously labelled 2-methyl-2-norbornanol (**2**) by ionization in FSO_3H/SbF_5. The cation was generated by adding dropwise a precooled solution of the alcohol in SO_2ClF to a vortex-stirred solution of 1:1 FSO_3H/SbF_5 in SO_2ClF at 143 or 195 K. A highly deshielded signal at about δ_C 269 is found for the C-2 cation centre of (**1**).[4] Figure 1 shows ^{13}C spectra of the C-2 region for two mixtures of isotopomers in which each isotopomer bears a single deuterium at a different position in the ring structure. In Figure 1(a), all ten possible isotopomers were present in solution, as well as a small amount of the unlabelled cation.† The position of the C-2 signal for unlabelled (**1**) was identified

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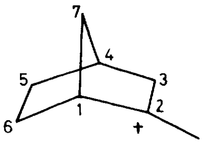
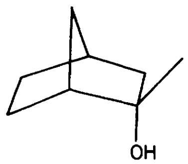
† This randomly labelled alcohol precursor was prepared by a 4-step synthesis, starting from treatment of a mixture of nortricyclene and norbornylene (2:1) with $MeCO_2D/D_2SO_4$, followed by lithium aluminium hydride reduction of the 2-norbornyl acetate, oxidation to 2-norbornanone with pyridinium chlorochromate/CH_2Cl_2, and addition with methylmagnesium bromide. Mass spectra of the resulting mixture indicated about 90% of monodeuteriated and 10% unlabelled (**2**).



(1)



(2)

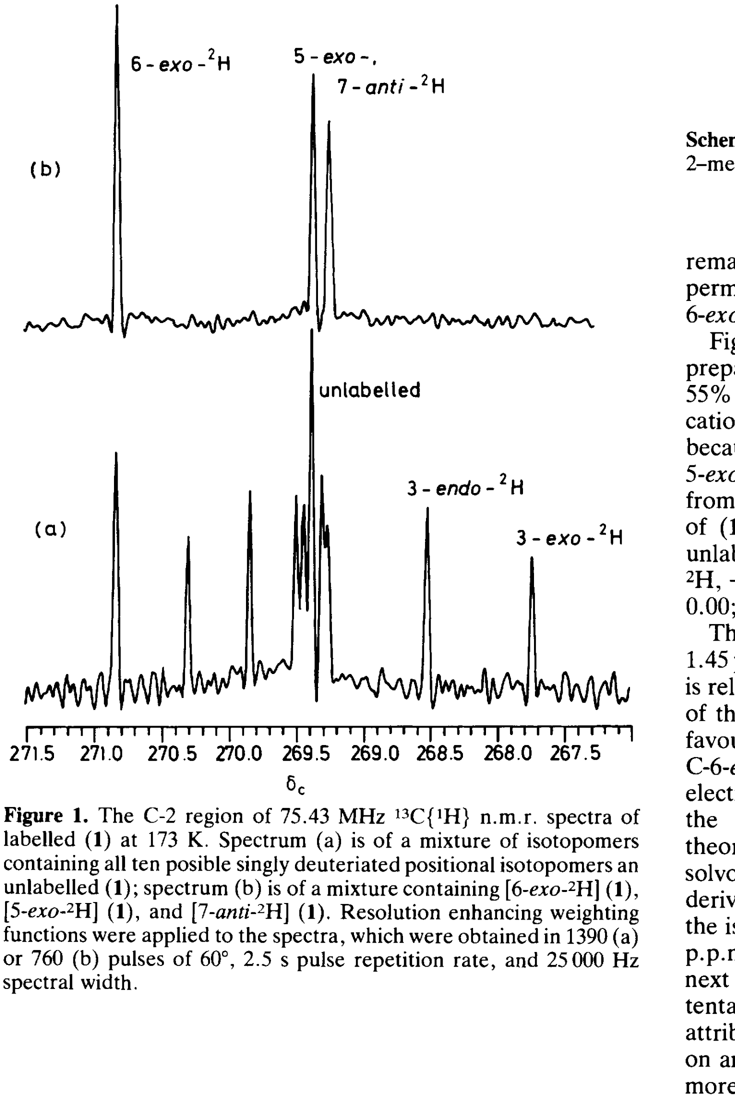
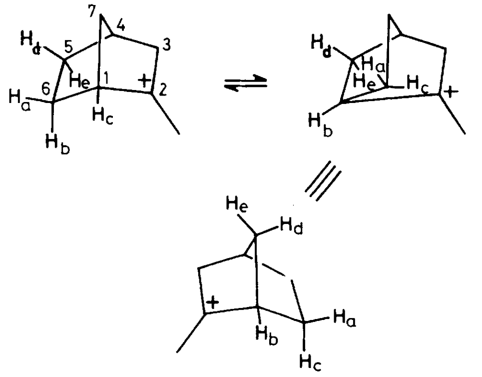


Figure 1. The C-2 region of 75.43 MHz $^{13}C\{^{1}H\}$ n.m.r. spectra of labelled (**1**) at 173 K. Spectrum (a) is of a mixture of isotopomers containing all ten posible singly deuteriated positional isotopomers an unlabelled (**1**); spectrum (b) is of a mixture containing [6-*exo*-^{2}H] (**1**), [5-*exo*-^{2}H] (**1**), and [7-*anti*-^{2}H] (**1**). Resolution enhancing weighting functions were applied to the spectra, which were obtained in 1390 (a) or 760 (b) pulses of 60°, 2.5 s pulse repetition rate, and 25 000 Hz spectral width.

by comparison with the spectrum of a sample containing additional unlabelled (**1**). The upfield C-2 signals for [3-*exo*-^{2}H] (**1**) and [3-*endo*-^{2}H] (**1**) were assigned previously.[1]

It is not a simple matter to assign unequivocally most of the isotopically shifted C-2 signals. Even if (**1**) were prepared from ten different specifically labelled precursors, assignment would not be complete because a rapid rearrangement partially scrambles the label before measurement is possible, even at 143 K.[1,5] The rearrangement, shown in Scheme 1, may be considered as proceeding *via* a simple 6,1-hydride shift in a partially bridged ion (or in classical terms, *via* a sequence of Wagner–Meerwein rearrangement, 6,2-hydride shift, and another W–M rearrangement). The rearrangement equilibrates the 5-*exo*-^{2}H and 7-*anti*-^{2}H isotopomers; similarly paired are the 3-*exo*-^{2}H and 3-*endo*-^{2}H, 5-*endo*-^{2}H and 7-*syn*-^{2}H, and 6-*endo*-^{2}H and 1-^{2}H isotopomers. However, the 6-*exo* label remains at that position in this facile rearrangement, thus permitting unequivocal identification of the signal for the 6-*exo*-^{2}H isotopomer.



Scheme 1. Rearrangement which exchanges pairs of hydrogens in the 2–methyl–2-norbornyl cation.[1,5]

Figure 1(b) shows the C-2 region of the spectrum for (**1**) prepared from a sample of (**2**) containing 40% [6-*exo*-^{2}H] (**2**), 55% [5-*exo*-^{2}H] (**2**), and 5% unlabelled (**2**).‡ In the resulting cation mixture, the 6-*exo*-^{2}H isotopomer is the most abundant because the initial 5-*exo*-^{2}H label is distributed between the 5-*exo* and -*anti* positions through the rearrangement. Thus, from Figure 1 and the previous study,[1] the isotope shifts at C-2 of (**1**) at 173 K are (isotopomer, p.p.m. shift relative to unlabelled compound at δ_C 269.4): 3-*exo*-^{2}H, −1.64; 3-*endo*-^{2}H, −0.85; 6-*exo*-^{2}H, 1.45; 5-*exo*-^{2}H and 7-*anti*-^{2}H, −0.12 and 0.00; unassigned, 0.91, 0.46, 0.11, 0.06, and −0.08.

The observation of an unusually large isotope effect, the 1.45 p.p.m. downfield shift, associated with a 6-*exo*-deuterium is relevant to current discussion surrounding the exact nature of the non-classical bonding in 2-norbornyl cations.[6,7] Grob favours a model with direct bridging from C-6 and in which the C-6-*exo*-H electrons are particularly important because of electron donation through the backside lobe of the orbital for the 6-*exo* bond.[7] Grob's model has been criticized on theoretical grounds and because secondary isotope effects in solvolysis of [6-*exo*-^{2}H] and [6-*endo*-^{2}H] 2-*exo*-norbornyl derivatives are nearly identical.[6] Without presuming to settle the issue, we find it noteworthy that the isotope shift of 1.45 p.p.m. at C-2 in [6-*exo*-^{2}H] (**1**) is considerably larger than the next largest downfield isotope shift of 0.91 p.p.m. which we tentatively assign to [6-*endo*-^{2}H] (**1**). In general terms, we attribute the large isotope shifts in (**1**) either to isotope effects on an equilibrium between an open and a bridged cation, or more likely, to perturbation of vibrational motion over a shallow energy surface associated with the bridging co-ordinate in a partly bridged ion.[2] Recent theoretical calculations of ^{13}C chemical shifts in carbocations support previous interpretations that shielding is associated with bridging.[8] The perturbation associated with a 6-*exo*-deuterium in (**1**) is apparently away from bridging towards a more open ion giving a more deshielded cation centre, while labelling at the 3-position perturbs the structure towards more bridging and shielding of the cation centre.

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‡ Labelling with a single deuterium at either the 5-*exo* or 6-*exo* positions of (**2**) was achieved by the key step, deuteriation of 2-(5-norbornenyl)benzyl ether with $NaBD_4$ and BF_3–ether in diglyme, followed by treatment with acetic acid. The resulting mixture was debenzylated to give a mixture of [5-*exo* and 6-*exo*-^{2}H]norbornan-2-ol] which was then treated in the same manner mentioned in ref. 3.

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