FTIR spectra of matrix isolated 2-methylbenzonorbornen-2-yl-type cations

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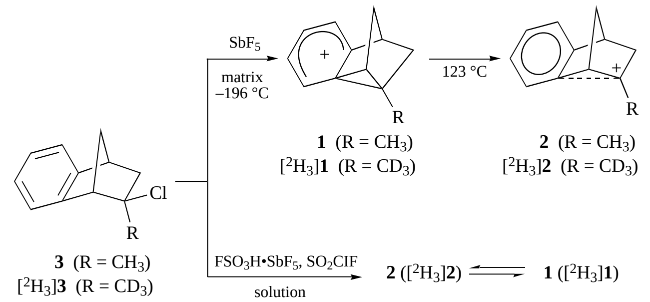
FTIR spectra suggest that ionization of 2-*exo*-chloro-2-methylbenzonorbornene† in an SbF_5 matrix at −196 °C leads to 2-methyl-2-benzonortricyclyl cation which rearranges into a partially π-bridged 2-methylbenzonorbornen-2-yl ion at −123 °C.

2-Methylbenzonorbornen-2-yl cation has been recently reinvestigated[1] by ^{13}C NMR spectroscopy by substituting deuterium for hydrogen in the methyl group and temperature variation. It has been concluded that this cation in $FSO_3H{\cdot}SbF_5$–SO_2ClF solution is in fact not a static ion (*cf.* refs. 2 and 3), but a dynamic system of very fast equilibrating ions **1** and **2** differing in positive charge delocalization. However, the fine structures of the cations **1** and **2** remained unknown. Now we report on the study of these cations by FTIR spectroscopy using the matrix isolation method with SbF_5 as a matrix material.

Matrices were prepared by co-condensation of 2-*exo*-chloro-2-methyl- or 2-*exo*-chloro-2-trideuteriomethyl-benzonorbornene (**3** or [$^2H_3$]**3**) and SbF_5 on a cryogenic CsI window. The FTIR spectra obtained suggest that the ionization of the chloride **3** ([$^2H_3$]**3**) at −196 °C leads to the benzenium-type carbocation **1** ([$^2H_3$]**1**) (Scheme 1). It follows from the appearance of new strong bands in the C=C stretching area (1598 cm^{-1} for **1** and 1594 cm^{-1} for [$^2H_3$]**1**) (Fig. 1) and the bands which may be due to the cyclopropane rings of the cations (1005 and 1008 cm^{-1}, respectively). Note that the intensity of the C=C stretching bands increases significantly in going from the precursors **3** and [$^2H_3$]**3** to the ions. Such a change in intensity is an indication for polarized C=C bonds in the benzenium carbocations. The C–D stretching frequency for [$^2H_3$]**1** is equal to that for chloride [$^2H_3$]**3** (2224 cm^{-1}).



Scheme 1

Warming the matrices to −123 °C results in a complete transformation of the spectra, the new spectra being unchanged up to −10 °C. They contain strong bands in the C=C stretching region (1604 cm^{-1} for the non-deuteriated species and 1613 cm^{-1} for the deuteriated species). A band at 2066 cm^{-1} due to C–D stretching is also observed in the spectrum of the deuteriated cation. The observed changes in the spectra are apparently due to the transformation of the cations **1** and [$^2H_3$]**1** into carbocations of benzonorbornenyl-type **2** and [$^2H_3$]**2**, respectively.

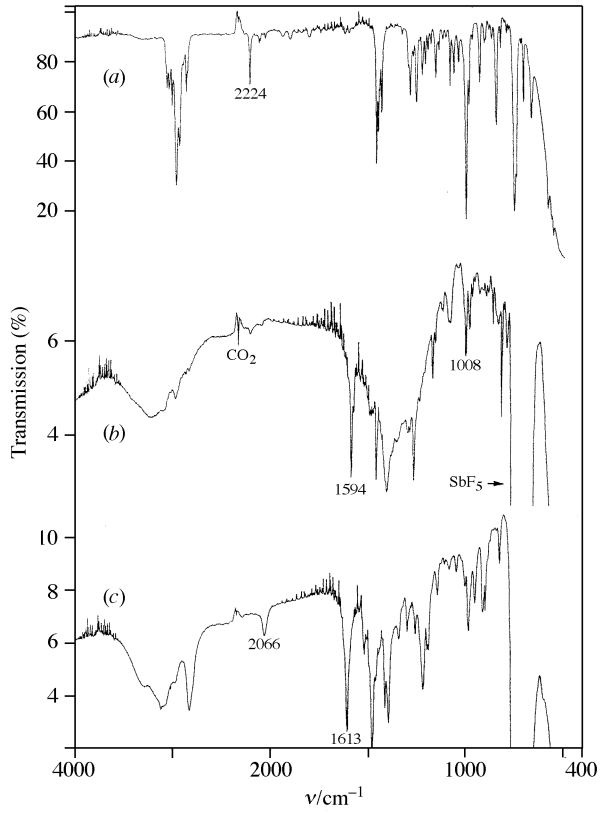


Fig. 1 FTIR spectra of [$^2H_3$]**3**: starting compound (*a*) at room temperature, (*b*) in a SbF_5 matrix at −196 °C and (*c*) in a SbF_5 matrix at −123 °C

The C=C stretching frequencies for both **1** ([$^2H_3$]**1**) and **2** ([$^2H_3$]**2**) are close to those of benzenium ions[4] (*ca.* 1600 cm^{-1}). The lower frequency for **1** ([$^2H_3$]**1**) than for **2** ([$^2H_3$]**2**) can be explained by greater electron withdrawal from the benzene ring in the former. The C–D stretching frequency significantly diminished in the cation [$^2H_3$]**2** relative to the precursor, chloride [$^2H_3$]**3** (from 2224 to 2060 cm^{-1}). This low frequency shift is obviously due to the hyperconjugation of the CD_3 group attached to the C-atom bearing a significant positive charge. Similar vibrational hyperconjugative effects were observed earlier.[5,6] Note that such a shift is not observed for [$^2H_3$]**1** where the C-2 atom is not a trigonal cationic centre.

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† IUPAC name for benzonorbornene is 1,2,3,4-tetrahydro-1,4-methanonaphthalene.

The following conclusions on the fine structures of the cations **1** ($[^2H_3]$**1**) and **2** ($[^2H_3]$**2**) may be derived from the above data: the structure of **1** ($[^2H_3]$**1**) is rather close to that of a phenonium-like cation; the fine structure of **2** ($[^2H_3]$**2**) remains to be determined, but it is clear that π-bridging affects this ion.

Of particular note are the differences in the energy surface of the 2-methylbenzonorbornen-2-yl ion in $FSO_3H{\cdot}SbF_5$–SO_2ClF solution and in the SbF_5 matrix. In solution, the ions **1** and **2** are of near equal stability and the free energy barrier between them is very low (less than 20 kJ mol^{-1} at -127 °C).[1] In the matrix, the ion **2** is much more stable than **1**, the barrier of the rearrangement **1**→**2** being higher than 40 kJ mol^{-1} (*cf.* ref. 7).

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