Structures of Radical Cations of Norbornane and Norbornadiene: E.S.R. Evidence

Kazumi Toriyama, Keichi Nunome, and Machio Iwasaki*

Government Industrial Research Institute, Nagoya, Hirate, Kita, Nagoya 462, Japan

The radical cations of norbornane and norbornadiene have been generated radiolytically in Freon matrices at 4.2 K; the unpaired electron orbitals of these cations were identified as the $4a_2$ σ_{CC} and $6b_2$ π_{CC} orbital, respectively.

Norbornane and norbornadiene, the most typical strained bicyclic alkane and alkene, respectively, are of fundamental importance in the study of such strained ring compounds, which has attracted considerable interest.[1] In a continuation of our studies of radical cations of alkanes and related compounds,[2–4] the radical cations of norbornane and norbornadiene have been identified by e.s.r. spectroscopy for the first time.

The radical cations were produced radiolytically in $CFCl_2CF_2Cl$[2b] as well as in $CFCl_3$.[5] The irradiation was carried out at 4.2 K with *X*-rays (45 kV, 40 mA), since irradiation at 77 K often results in secondary changes of the initial structure of radical cations.[2c] Figure 1(a) shows the e.s.r. spectrum of norbornane cation radicals formed in $CFCl_2CF_2Cl$. The spectrum observed in $CFCl_3$ was essentially the same. The equally spaced five-line spectrum [coupling constant of 65.1 G (in $CFCl_2CF_2Cl$) and 66.8 G (in $CFCl_3$)] with a binomial intensity ratio indicates that the SOMO must involve the four equivalent protons. The candidates, expected from molecular symmetry, are four *exo* or *endo* protons. If the *exo* protons are taking part, the SOMO must be the $4a_2$ σ_{CC} orbital (I), in which the C–H_{exo} σ bonds participate more preferentially in the SOMO than the C–H_{endo} bonds, which are almost perpendicular to the unpaired σ_{CC} orbitals.[6] The tertiary protons in the $4a_2$ SOMO are similar in nature to π-protons so that the small α-proton coupling may only contribute to the linewidth. As for the C–H protons at C-7, hyperconjugation must be symmetry forbidden giving essentially zero coupling.

If the *endo* protons are taking part, the $7b_1$ π_{CC} orbital (II) may give a large coupling to the endo C–H protons.[6] However, INDO calculations using the geometry determined by electron diffraction[7] indicates that the SOMO is $4a_2$ rather

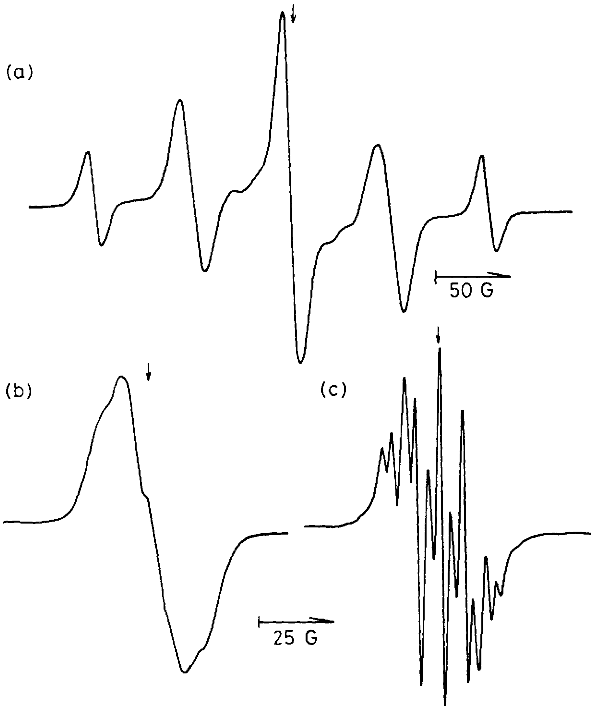
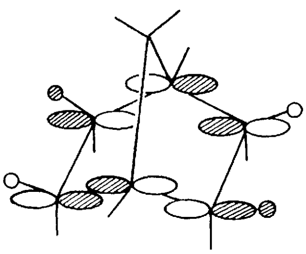
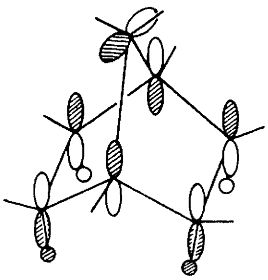


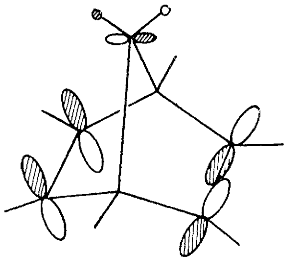
Figure 1. E.s.r. spectra of the radical cations of (a) norbornane observed at 4.2 K; (b) norbornadiene observed at 77 K; and (c) norbornadiene observed at 100 K, in a $CFCl_2CF_2Cl$ matrix. The samples were irradiated with *X*-rays at 4.2 K. The spectrum of the norbornadiene cations at 4.2 K is essentially the same as that at 77 K. The arrows indicate the position of the diphenylpicrylhydrazyl marker. 1 G = 10^{-4} T.



$4a_2$
(I)



$7b_1$
(II)



$6b_2$
(III)

than $7b_1$. In addition, the calculated *exo* proton coupling, 65.0 G, is in good agreement with the observed values (65.1 G and 66.8 G) with all the rest of the protons giving coupling constants of <5 G. The square of the coefficient of the *endo* protons in the $7b_1$ orbital (II) is smaller by a factor of 0.7 than that of the *exo* protons in the $4a_2$ orbital. *Ab initio* calculations on norbornane also show that the highest and second highest occupied orbitals are $4a_2$ and $7b_1$, respectively, and the coefficient of the *endo* protons in the $7b_1$ orbital is much smaller than that of the *exo* protons in the $4a_2$ orbital.[6]

These results suggest that the radical cation of norbornane possesses the unpaired electron in the $4a_2$ SOMO and the four *exo* protons are responsible for the five-line spectrum. The extremely large hyperfine coupling (*ca.* 65 G) to the *exo* protons is due to σ-delocalization to the *exo* C–H σ bonds, similar to the in-plane terminal C–H protons in propane cations.[2a] The results are in agreement with the σ-delocalization to the equatorial protons existing in cycloalkane cation radicals.[4]

The radical cations of norbornadiene in $CFCl_2CF_2Cl$ gave a 5 × 3 line spectrum with coupling constants of 8.0 G (4H) and 3.3 G (2H), Figure 1(c). Essentially the same spectrum was obtained in $CFCl_3$. The small coupling constants are typical of delocalized π radicals, in contrast to the σ-delocalized radicals of norbornane. The four equivalent protons are clearly the protons attached to the basal carbon atoms. Since the tertiary C–H bonds have a dihedral angle of approximately 90° with respect to the unpaired electron orbital, essentially zero coupling is expected. So, the two equivalent protons with a coupling constant of 3.3 G must be the two protons at C-7, with which a large through-space-interaction is expected. Thus, it is concluded that the radical cations of norbornadiene possess the unpaired electron in the $6b_2$ orbital (III).[8] Our INDO calculation using a considerably elongated C=C bond distance (1.443 Å) revealed a $6b_2$ SOMO with reasonable coupling constants for both the basal (-5.8 G) and the C-7 (2.1 G) protons.

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