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Nuclear Quadrupole Resonance in *syn*- and *anti*-7-Chloronorbornene

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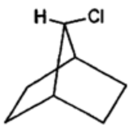
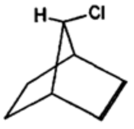
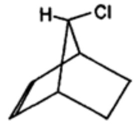
Norbornenyl halides and other derivatives show unusual rate effects in their solvolysis reactions:[1] *syn*-7-chloronorbornene (II) and its saturated analog (I) solvolyze in aqueous ethanol at comparable rates, whereas the *anti*-isomer (III) solvolyzes some 10^5 faster than I and II under the same conditions.[2] These and other large variations in the reaction rate in norbornenyl systems have been interpreted in terms either of the "*participation*" of the neighboring π-bond electrons in the initial carbonium ion formation or of some modification of the bridgehead molecular structure due to steric effects of the large substituents.[1]



I



II



III

To examine if such isomeric rate effect is associated with the nature of the C–Cl bonds or the valence state of carbon atom, we have measured the nuclear quadrupole resonance frequencies of ^{35}Cl in II and III. The details of the experimental procedures have been reported.[3]

The experimental results are given in Table 1, from which we recognize that two crystallographically nonequivalent molecules exist in each of the compounds II and III. The mean value of the resonance frequencies in II is some 860 kHz larger than that of III but their absolute values fall in the range generally found in compounds of the type $(CH_3)_nCH_{3-n}Cl$.[4] This means that the C–Cl bonds in II and III themselves are not unusual. On the other hand, the difference in the resonance frequencies in II and III seems to be significant,

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[1] H. Tanida, *Accounts of Chemical Research*, **1**, 239 (1968) and the references therein.

[2] W. G. Woods, R. A. Carboni and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).

[3] H. Chihara, N. Nakamura, H. Ōkuma and S. Seki, This Bulletin, **41**, 1809 (1968).

[4] E. I. Fedin and G. K. Semin, "Use of Nuclear Quadrupole Resonance in Chemical Crystallography II," in "The Mössbauer Effect and its Applications in Chemistry," Consultants Bureau Enterprises, Inc., New York (1964).

TABLE 1. THE NUCLEAR QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl AT LIQUID NITROGEN TEMPERATURE

Substance	Resonance frequency (kHz)
syn-7-Chloronorbornene (II)	33016.3 ± 0.2 33026.2 ± 0.1
anti-7-Chloronorbornene (III)	32125.2 ± 0.1 32191.4 ± 0.1

because the intermolecular contributions to the NQR frequencies of chlorine bonded to carbon atoms are relatively small and vary regularly from compound to compound.[5)]

The difference between the mean resonance frequencies of II and III may be attributed to a change in the hybridization of the C–Cl bond. Thus, in the case of simple molecules such as $CH_{4-n}X_n$ and $(CH_3)_nCH_{3-n}X$ (X=Cl, Br or I), it can easily be confirmed from $J(^{13}C\text{–}H)$ data[6)] or from molecular geometry that the halogen nuclear quadrupole coupling constant in C–X bond increases with an increase in the *s*-character of the carbon atomic orbital bonded to the halogen atom.[7)] On applying this relation to the case of the compounds II and III, we see that the *s*-character of the carbon atomic orbital in the C–Cl bond in II is larger than that in III and this trend agrees qualitatively with the direction of the shift of $J(^{13}C\text{–}H)$ observed in these two compounds[8)] and in some similar compounds.[9)] Such a difference in the carbon *s*-character is probably due to distortion of the C–Cl bond originating from the repulsion between the bulky chlorine atom and the carbon π-orbital in II although some delocalization of the π-electrons in III cannot be entirely excluded.[9)]

Although both the NQR frequencies and $J(^{13}C\text{–}H)$ data can be explained consistently by the change in the carbon hybridization as mentioned above, the question of how the large reaction rate effect in 7-norbornenyl system can be interpreted by such a mechanism remains unclarified.

Another explanation for the difference of the NQR frequencies is to assume that a weak hydrogen bond is operating between the bridge carbon and the π-electrons. This makes the chlorine in III more electronegative than in II *via* the inductive effect between the hydrogen and the chlorine. In other words the chlorine in III is more ionic than in II and is more susceptible to solvolysis. Actually these two alternative explanations are compatible and are probably both correct. Though their relative significance is unknown, they complement each other in making the chlorine resonance displaced to a lower frequency in III.

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5) See, for example, D. Biedenkapp and A. Weiss, *Ber. Bunsenges. Physik. Chem.*, **70**, 788 (1966); W. J. Considine, *J. Chem. Phys.*, **44**, 4036 (1966).

6) The *s*-character of the carbon hybrid orbital involved in the C–H bond is proportional to $J(^{13}C\text{–}H)$; see C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

7) A qualitative account for the relation between the carbon *s*-character and the NQR frequencies is as follows: From the point of view of Jaffe's electronegativity scheme (J. Hinze *et al.*, *J. Am. Chem. Soc.*, **84**, 540 (1962); *ibid.*, **85**, 148 (1963)), the increase in the *s*-character of the carbon orbital tends to increase the carbon orbital electronegativity. Therefore, the amount of the electron transfer, necessary for matching the orbital electronegativities, from the carbon hybrid orbital to the chlorine orbital may decrease and so the number of the unbalanced *p*-electrons at the chlorine increases, with the result of a higher NQR frequency.

8) M. Ueyama and K. Tori, private communication. The coupling constants, $J(^{13}C\text{–}H)$'s, between the bridge carbon and the hydrogen bonded to it were determined to be 156.5±1 Hz and 164.2±1 Hz for II and III, respectively.

9) K. Tori, S. Sato, T. Tsushima and H. Tanida, Abstract for the 6th Conference on Nuclear Magnetic Resonance, Kyoto (1967).