

CHLORINE NQR SPECTRA OF CHLORONORBORNANES AND CHLORONORBORNENES¹

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Abstract— Cl^{35} nuclear quadrupole resonance (NQR) spectra are reported for a number of chloronornornanes and chloronornornenes and assignments suggested. The NQR "chemical shifts" seem to be additive functions of structure, suggesting that measurements of this kind may be of value in determining the structures of such compounds.

INTRODUCTION

NUCLEAR quadrupole resonance (NQR) spectroscopy² is a well established but somewhat neglected procedure whereby valuable information can be obtained concerning chemical bonding. The original objective of the present investigation was to see if information could be obtained in this way that might have a bearing on the "non-classical carbonium ion" problem.³

In saturated chlorine compounds, the Cl^{35} NQR frequency is usually a measure of the charge on chlorine, and the frequency can accordingly be altered by the presence of "inductive" substituents. Thus introduction of successive Me groups into MeCl leads to a uniform decrease⁴ in the NQR frequency along the series MeCl, 34.023 MHz; EtCl, 32.705 MHz; *i*-PrCl, 31.939 MHz; *t*-BuCl, 31.065 MHz (at liquid nitrogen temperature). Since phenyl is electron withdrawing relative to hydrogen, one would expect the frequency for benzyl chloride to be greater than that for methyl chloride; in fact it is less (33.627 MHz). This discrepancy is undoubtedly due to a hyperconjugative interaction between the π MOs of the ring and the carbon-chlorine σ bond MO which has the effect of increasing the electron density in the carbon-chlorine bond region. In resonance terminology, this would be represented in terms of a contribution by the ionic structure ($\text{PhCH}_2^+ \text{Cl}^-$). The hyperconjugative interaction symbolized in this way is obviously analogous to the resonance interaction between phenyl and methylene that stabilizes the benzyl cation, PhCH_2^+ , an interaction which is responsible for the ease with which benzyl chloride undergoes $\text{S}_{\text{N}}1$ reactions. One might on this basis expect similar hyperconjugative interactions to be important in other compounds RCl where R can form a stable ion R^+ . Our original purpose was to look for this effect in chlorides which solvolyse easily and whose high rate of solvolysis had been attributed³ to the intervention of π -complexes or other "non-classical carbonium ions". Here of course the ease of solvolysis of a chloride RCl is being attributed to stability not of the ion R^+ itself, but of a rearrangement product R_1^+ ; however the same factors that lead to stabilization of the latter might con-

ceivably also affect the CCl bond in RCl, by an interaction that could be represented in terms of resonance theory as a contribution by the resonance structure (R^+Cl^-).

It therefore seemed to us of obvious interest to study the NQR spectra of appropriate chloro derivatives of norbornane and norbornene. This project seemed even more attractive because one of us (A.P.M.) had prepared a number of such compounds in another connection and because a number of polychlorinated norbornane derivatives are known to be useful insecticides. It seemed to us that a study of the NQR spectra of such compounds, apart from its theoretical interest, might lead to results of possible practical value in determining structures.

While this work was in progress, ^{35}Cl NQR spectra for two key compounds (*syn* (I) and *anti* (II) 7-chloronorbornene) were reported by other workers.⁵ The coupling constant for II (32.158 MHz) was significantly less than that (33.021 MHz) for I, implying that a backside interaction of the π electrons with the CCl bond does indeed lead to increased ionic character of Cl in II. Since our results are relevant in this connection, and also in the other indicated above, we are reporting them.

RESULTS

The compounds studied are listed in Fig. 1. Table 1 shows measured frequencies of the NQR transitions.

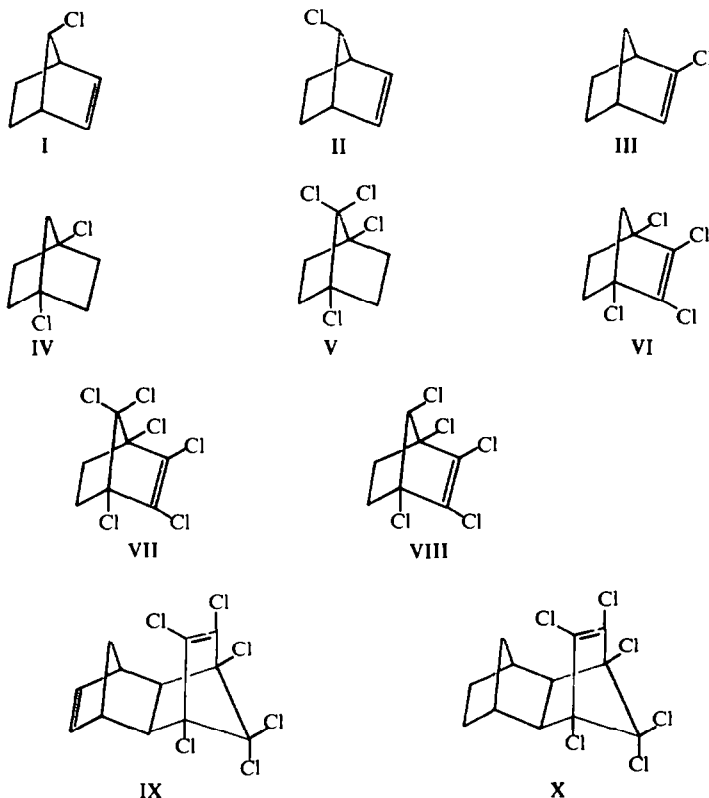


FIG. 1. Structures of compounds studied

TABLE I. Cl^{35} NQR SPECTRA OF NORBORNANE DERIVATIVES.

Compound	NQR Frequency (MHz)	Signal/noise ratio
2-Chloronorbornene (III)	33·762 ± 0·003	5
1,4-Dichloronorbornane (IV)	32·980 ± 0·001	3
	33·170 ± 0·001	3
1,4,7,7-Tetrachloronorbornane (V)	34·484 ± 0·001	4
	35·255 ± 0·0003	3
	37·315 ± 0·002	11
1,2,3,4-Tetrachloronorbornene (VI)	34·981 ± 0·001	3
	35·482 ± 0·001	3
	36·297 ± 0·001	4
	36·385 ± 0·002	4
	36·498 ± 0·001	4
1,2,3,4,7,7-Hexachloronorbornene (VII)	36·295 ± 0·0003	3
	36·885 ± 0·005	5
	37·741 ± 0·001	4
	38·401 ± 0·002	4
1,2,3,4- <i>syn</i> -7-pentachloronorbornene (VIII)	35·777 ± 0·003	3
	36·051 ± 0·001	3
	36·308 ± 0·001	3
	36·465 ± 0·001	3
	36·724 ± 0·002	4
Aldrin (IX)	36·683 ± 0·001	4
	<i>ca.</i> 38·485	2
Dihydroaldrin (X)	36·265 ± 0·001	3
	36·564 ± 0·001	3
	36·766 ± 0·001	3
	37·087 ± 0·0003	3
	37·746 ± 0·0003	3
	38·190 ± 0·001	2
	<i>ca.</i> 38·853	2
<i>ca.</i> 38·978	2	

Assignment of Transitions

The effect of substituents on the Cl^{35} NQR frequency of alkyl chlorides has been thoroughly studied;² in the absence of conjugative or hyperconjugative (*cf.* PhCH_2Cl) interactions, the "chemical shifts" seem to be additive. Thus in the series⁴ MeCl , EtCl , *i*- PrCl , *t*- BuCl , the NQR frequency falls by decrements of 1·32, 0·77, and 0·87 MHz, while in the series CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 the frequency rises by increments of 1·97, 2·29, and 2·35 MHz. The scatter in each case can be attributed to varying crystal field effects; these can easily lead to differences of 0·3 MHz between signals for compounds where the chlorine atoms would be expected to be equivalent.

The following assignments of transitions to individual chlorine nuclei in III-X are made on the assumption that similar additivity holds. It also seems reasonable to expect a reciprocal relation to hold between pairs of chlorine nuclei, the chemical shifts of each, due to their mutual interaction, being the same.

The Cl^{35} frequency for III is close to that for vinyl chloride (33.414 MHz⁸); however III is a derivative of an α -alkylated vinyl chloride so one might have expected the frequency to be correspondingly less than that for vinyl chloride itself. While no data are available for the effect of an α -alkyl substituent on vinylic chlorine, one might have expected it to be similar to that in saturated systems, i.e. *ca.* 1.0 MHz. In that case the frequency for III is about 1 MHz greater than would have been expected. A possible explanation of this can be given in terms of ring strain in III. The bond angles in the ring at the olefinic carbon atoms must be much less than the equilibrium value of 120°; the 123 bond angle in III has indeed been estimated to be 109–110°.⁹ This should tend to decrease the *s*-character of the orbitals used by the olefinic carbon atoms to form σ bonds to adjacent atoms in the ring, and so correspondingly increase the *s*-character of the orbital used to form the external bonds. Since an increase in *s*-character implies an effective increase in electronegativity, this effect should tend to make the CCl bond in III less polar and so increase the NQR frequency. The same effect seems to operate in the case of IV where the observed frequency (33.075 MHz; mean of observed crystal field doublet) is much greater than that for an acyclic tertiary chloride (e.g. *t*-BuCl, 31.065 MHz⁴). The bond angles at the bridgehead in IV are much less¹⁰ (92.8° and 104.4°) than in *t*-butyl chloride¹¹ (111.5°).

The assignment of frequencies for V is unambiguous since the higher frequency (37.315 MHz) must correspond to the CCl_2 group, the difference from IV being much too great to be attributed to an "inductive" effect of CCl_2 on the bridgehead chlorine. The two other transitions must then arise by crystal field splitting of the transition for the tertiary chlorines (mean, 34.87 MHz). The signal for these is thus shifted by +1.8 MHz relative to IV, by the chlorine atoms in the 7-positions. If it can be assumed that the chlorine-chlorine interactions follow a reciprocal relation, one arrives at an estimate of 35.5 MHz for the n.q.r. frequency of 7,7-dichloronorborene. Comparison with I then indicates that the mutual interaction of the chlorine atoms in 7,7-dichloronorborene increases the n.q.r. frequency by 2.50 MHz.

In VI, the two lower frequencies must represent a crystal field doublet (mean, 35.23 MHz), and the three higher ones (mean, 36.39 MHz) a crystal field triplet. Since the vinylic chlorines each have two chlorine atoms adjacent to them, while the tertiary chlorines are each adjacent to only one other chlorine, one would expect the shift of the vinylic chlorines, relative to III, to be greater than that of the tertiary chlorines relative to IV. Since the Cl^{35} frequency for III is greater than that for IV, the higher frequency signal for VI (36.39 MHz) must correspond to the vinylic chlorines and the lower (35.23 MHz) to the tertiary ones. If the interactions between adjacent chlorines follow a reciprocal relation, one would deduce values of 2.16 MHz for the vinyl-bridgehead interaction and +0.57 MHz for the vinyl-vinyl one. The former value seems rather large for a 1.2 interaction; it is possible that there may be a significant 1.3 interaction between chlorine atoms in the system $\text{Cl}-\overset{\text{Cl}}{\underset{|}{\text{C}}}-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\overset{\text{Cl}}{\underset{|}{\text{C}}}-\text{Cl}$, the net value of 2.16 MHz being a sum of 1.2 and 1.3 interactions. There do not seem to be data available to resolve this point.

The frequency for the bridgehead chlorines in VII can be estimated from the values in V or VI by using the parameters derived above; the two estimates (37.03 and 37.03 MHz) agree exactly. The signal at 38.40 MHz must then correspond to the CCl_2 group; the difference between this value and that (37.32 MHz) for CCl_2 in V must be attributed to a 1.3 interaction with the vinylic chlorines. The corresponding interaction parameter is then 0.54 MHz. Using this, we find a predicted frequency of 37.48 MHz for the vinyl chlorines in VII. The signal at 37.74 MHz can thus be attributed to the vinyl chlorines, and the other two frequencies (mean, 36.59 MHz) to the bridgehead ones.

Using these interaction parameters, we arrive at the following estimates of frequencies for VIII:

$$7, \text{Cl } 35.90; 1(4), \text{Cl } 36.13; 2(3)\text{Cl}, 36.94 \text{ MHz}$$

These results suggest that the signal at 36.72 MHz corresponds to the vinylic chlorines, those at 36.31 and 36.47 (mean, 36.39 MHz) to the bridgehead chlorines, and those at 35.78 and 36.05 (mean, 35.91 MHz) to the 7-chlorine.

The spectrum of IX was too poorly resolved to permit identification of the signals; that at 38.48 MHz presumably corresponds to the CCl_2 group. The spectrum of X should, according to the present approximation, be similar to that of VII; the following assignment seems plausible, the frequencies for VII being given in parentheses:

$$\begin{aligned} \text{CCl}_2 &: 38.190, 38.853, 38.978; \text{ mean } 38.67 \text{ MHz } (38.40) \\ \text{vinylic Cl} &: 37.087, 37.746; \text{ mean } 37.42 \text{ MHz } (37.47) \\ \text{bridgehead Cl} &: 36.265, 36.564, 36.766; \text{ mean } 36.53 \text{ MHz } (36.59) \end{aligned}$$

DISCUSSION

The ^{35}Cl n.q.r. spectra of III–X can thus be interpreted in an apparently very satisfactory manner in terms of additive interactions between pairs of chlorine atoms that carry over from one molecule to another. If it is assumed that the interactions between chlorine atoms in the 1,3 and 2,4 positions are the same as between 2 or 3 and 7, (i.e. 0.54 MHz), we arrive at the following values for the interaction parameters:

$$1-7, 0.90; 1-2, 1.61; 1-3, 0.54; 2-3, 0.57; 2-7, 0.54; 7,7, 2.50$$

If this interpretation is accepted, it will be seen that there is no evidence for any splitting of the signal for the CCl_2 chlorine atoms. This certainly seems to support the interpretation⁵ of the differences between the n.q.r. frequencies of I and II as being due to backside interaction of the CCl bond electrons in IV with the π electrons of the double bond; for since this interaction involves transfer of charge from the double bond to the CCl bond, it would be expected to be inhibited by substituents (e.g. Cl) which make the double bond less nucleophilic.

EXPERIMENTAL

Materials. The synthesis of the compounds studied here has been reported elsewhere.⁶

Measurement of NQR spectra. The samples, sealed in glass ampoules, were cooled by lowering them slowly (overnight) into liquid N_2 ; all measurements were made at the temperature of liquid N_2 , using a coherence-controlled superregenerative Zeeman-modulated spectrometer similar to that of Peterson and Bridenbaugh.⁷ Frequency measurements were made with a Singer Panoramic SPA-1 spectrum analyser and an AN-URM-32 Frequency Meter, calibrated against standard frequency broadcasts from WWV.

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REFERENCES

- ¹ This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67
- ² E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, New York, N.Y. (1969)
- ³ M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.* **16**, 321 (1965)
- ⁴ R. Livingston, *J. Chem. Phys.* **19**, 1434 (1951); *J. Phys. Chem.* **57**, 496 (1952); B. P. Dailey, *J. Chem. Phys.* **33**, 1641 (1960)
- ⁵ H. Chihara, N. Nakamura, and T. Irie, *Bull. Chem. Soc. Japan* **42**, 3034 (1969)
- ⁶ A. P. Marchand and W. R. Weimar, Jr., *J. Org. Chem.* **34**, 1109 (1969)
- ⁷ G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instr.* **35**, 698 (1964); **36**, 702 (1965); **37**, 1081 (1966)
- ⁸ R. Livingston, *Phys. Rev.* **82**, 289 (1951)
- ⁹ P. Laszlo and P. V. R. Schleyer, *J. Am. Chem. Soc.* **86**, 1171 (1964)
- ¹⁰ J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Ibid.* **90**, 3149 (1968)
- ¹¹ O. Bastiansen and L. Smedvik, *Acta Chem. Scand.* **7**, 653 (1953)