A Chlorine NQR Study of Some Perchloro-compounds

Masao HASHIMOTO and Koichi MANO*

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe
**Research Institute for Atomic Energy, Osaka City University, Sumiyoshi-ku, Osaka*

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The NQR frequencies of chlorines in seven perchloro-compounds were measured at 77°K and above. The assignments of the frequencies were made for each compound. It was found that the resonance frequency is considerably influenced by the electrostatic repulsion between chlorine atoms due to the close Cl···Cl distances. For several compounds, the resonance was found to fade out at rather low temperatures.

Several investigations of the nuclear quadrupole resonance, NQR, of the chlorine nucleus in perchloro-compound, C_mCl_n, have been reported.[1-4] Recently, West and his co-workers applied the NQR method to the determination of the molecular structure of some perchloro-compounds.[5-8] Their study constituets an important chemical application of the NQR technique. In order for this application to be reliable, however, it is necessary to establish the correlations between the molecular structure and the NQR frequencies. In the present work, we measured and assigned the NQR frequencies of chlorines in seven perchloro-compounds (Fig. 1) for which the crystal or molecular structures have been well established.

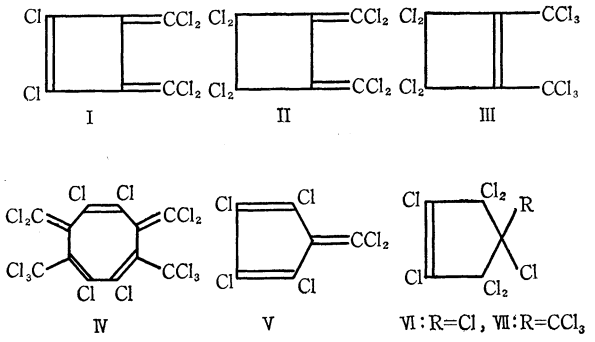

Fig. 1.

In perchloro-compounds, some of the chlorine atoms are expected to approach one another closely, because half or more than half of the atoms in the molecule are chlorine atoms. In fact, intramolecular and/or intermolecular Cl···Cl distances shorter than twice the van der Waals radius have been found in the crystals of some perchloro-compounds.[9-12] In this paper, we will report on the effect of the close Cl···Cl distance on the chlorine NQR frequency of perchloro-compounds. Agranat *et al.* have reported the effect of intramolecular interactions due to overcrowding on the NQR frequencies of chlorines in octachloropentafulvalene.[3]

Experimental

NQR Measurements. The NQR spectra were observed with an externally-quenched super-regenerative spectrometer; the absorption lines were displayed either on an oscilloscope or, when greater sensitivity was required, on a recorder after amplification by means of a lock-in amplifier. The frequencies were measured with a National VP-415 digital frequency counter. The accuracy of the frequency measurements was within ±2 KHz. The frequency measurements were carried out at 77°K (liquid nitrogen bath), at 198°K (dry ice-petroleum ether bath), and at room temperature. In some cases, the frequencies were measured at other temperatures by using a petroleum ether bath cooled by liquid nitrogen or dry ice. The temperature was determined by means of a copper-constantan thermocouple.

Materials. Perchloro-(3,4-dimethylenecyclobutene), I, was prepared by the dechlorination of perchloropropene with aluminum amalgam in ether.[13] This sample was purified by sublimation in a vaccum and by subsequent recrystallization from *n*-hexane under an atmosphere of nitrogen; mp 154—155°C.

Perchloro-(1,2-dimethylenecyclobutane), II, was prepared from I by means of chlorination with antimony pentachloride.[13] The sample of II was purified by chromatography on aluminum oxide. Recrystallization from acetone; mp 93°C.

Perchloro-(1,2-dimethylcyclobutene), III, was prepared from II by the same method as II. The product was purified by chromatography on aluminum oxide and by subsequent recrystallization from acetone; mp 153—154°C. The IR spectrum of this sample was identical with that of an authentic sample.[14]

Perchloro-(1,4-dimethyl-5,8-dimethylenecycloocta-1,3,6-triene), IV, was prepared from perchloro-(3,4,7,8-tetramethylenecyclooctadiene) by chlorination with liquid chlorine in a sealed tube.[13,15] It was then recrystallized from chloroform; mp 275°C.

Perchloro-(5-methylenecyclopentadiene), perchlorofulvene,[16] V, was obtained from perchloropropene by dechlorination with cuprous chloride in hydrous tetrahydro-

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Table 1. Measured frequencies for ^{35}Cl in some perchloro-compounds at various temperatures

Compound	No.	77°	198°K	Room temperature	Extrapolated value
		(Frequency in MHz)			
I	ν_1	38.066 (30.005)[a]	37.787		38.15
	ν_2	37.972 (29.936)	37.671		38.07
	ν_3	37.831 (29.822)	37.582		37.90
	ν_4	37.750 (29.758)	37.537		37.80
	ν_5	36.520 (28.783)	36.279		36.59
	ν_6	36.371 (28.663)	36.068		36.46
II	ν_1	38.839 (30.607)	38.527	38.144 (304°K)	38.94
	ν_2	38.639 (30.450)	38.292	37.881	38.75
	ν_3	38.072 (30.007)	37.701	37.292	38.18
	ν_4	37.901 (29.870)	37.634	37.252	38.00
III	ν_1	40.540 (31.953)	40.189	(298°K)	40.66
	ν_2	40.398 (31.953)	40.189		40.56
	ν_3	40.280 (31.753)	39.796		40.44
	ν_4	39.007 (30.742)	38.768	38.473	39.08
	ν_5	38.826 (30.600)	38.583	38.298	38.90
IV	ν_1	40.303 (31.769)	39.873	(294°K)	40.47
	ν_2	39.764 (31.344)	39.298		39.92
	ν_3	39.581 (31.199)	39.168		39.74
	ν_4	37.898 (29.871)	37.650	37.389	37.98
	ν_5	37.804 (29.794)	37.480	37.161	37.94
	ν_6	37.695 (29.710)	37.351	37.011	37.84
	ν_7	37.308 (29.406)	37.042	36.770	37.41
V	ν_1	38.314 (30.200)	38.002		38.41
	ν_2	38.190 (30.101)	37.852		38.31
	ν_3	38.094 (30.026)	37.755		38.21
	ν_4	37.806 (29.801)	37.514		37.94
	ν_5	37.169 (29.297)	36.928		37.27
	ν_6	36.792 (28.998)	36.570		36.89
VI[b]	ν_1	41.187	40.753	40.317 (293°K)	41.35
	ν_2	40.254	39.865	39.452	40.39
	ν_3	39.998	39.696	39.338	40.09
	ν_4	39.771	39.420	39.024	39.88
	ν_5	39.607	39.335	39.002	39.70
	ν_6	39.365	39.072	38.709	39.48
	ν_7	37.900	37.522	37.119	38.02
	ν_8	37.431	37.025	36.600	37.58
VII	ν_1	41.143 (32.432)	40.900	40.629 (300°K)	41.24
	ν_2	41.047 (32.355)	40.720	40.380	41.18
	ν_3	40.923 (32.254)	40.617	40.305	41.03
	ν_4	40.709 (32.086)	40.405	40.122	40.83
	ν_5	40.638 (32.031)	40.332	40.052	40.77
	ν_6	40.182 (31.670)	39.925	39.673	40.28
	ν_7	40.046 (31.562)	39.785		40.15
	ν_8	39.951 (31.484)	39.742	39.533	40.02
	ν_9	38.194 (30.105)	37.958	37.687	38.28
	ν_{10}	37.673 (29.697)	37.410	37.135	37.78

a) The value in ( ) is the measured frequency for ^{37}Cl.
b) Our results obtained for this compound at 77°K are in good agreement with the results of Semin *et al.* (Ref. 1).

furan.[17] The sample was identified by a comparison of the λ_{max} of its UV spectrum and its mp with the values reported for perchlorofulvene.[18] It was then purified by recrystallization from *n*-hexane at about 0°C. Deep-red needles; mp 155—156°C.

Perchlorocyclopentene, VI, was prepared by the chlorination of perchlorocyclopentadiene with antimony pentachloride.[13] Recrystallization from ethanol; mp 38—39°C.

Perchloro-(4-methylcyclopentene),[19] VII, was prepared from perchlorohexadiene-1,5 by treatment with anhydrous aluminum chloride in dichloromethane. Recrystallization from acetone; mp 133°C.

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Results and Discussion

The NQR frequencies of ^{35}Cl in these perchloro-compounds are summarized in Table 1, together with the frequencies of ^{37}Cl at 77°K.

The intensities of the resonance lines of II, III, IV, VI, and VII were found to be much stronger than those of I and V.

The number of resonance lines found for II and III was equal to half the number of chlorines in the corresponding molecule. This indicates that these molecules must possess one or more symmetry elements in their crystals.

In order to minimize the effect of lattice vibrations on the resonance frequency, the observed frequencies were extrapolated to 0°K. The extrapolated values are listed in the last column of Table 1.

The assignments of the frequencies are shown in Fig. 2.

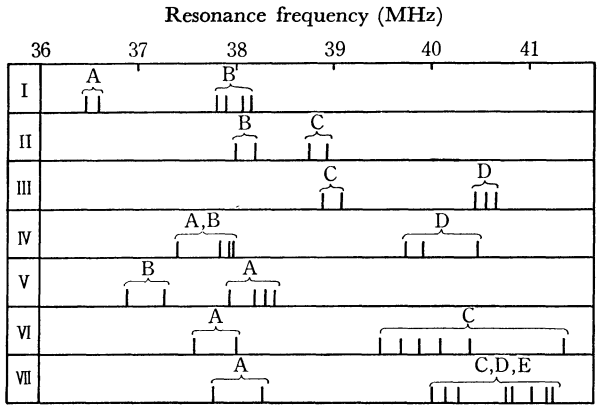

Fig. 2. Resonance frequencies extrapolated to 0°K. Vertical lines show the locations of the frequencies. The notations, A, B, C, D, and E, indicate the functional groups: A, $=\overset{|}{C}-Cl$: B, $=CCl_2$; C, $>CCl_2$, D, $-CCl_3$; E, $>\overset{|}{C}-Cl$.

The NQR spectrum of I consists of six resonance lines. Obviously these lines fall into two groups, one of two lines and one of four, centred at about 36.5 and 38.0 MHz respectively. From a structural point of view, the lower two lines may be attributed to the two vinyl chlorines attached to the cyclobutene ring, and the higher four lines, to the four chlorines in the two dichloromethylene groups. The frequencies of chlorines attached to the double bond in the cyclobutene ring are rather lower than those in the five- and eight-membered rings (see the spectra of IV, V, VI, and VII). Roedig *et al.* have reported unusually low resonance frequencies of vinyl chlorines on a cyclobutene ring, 35.53 and 35.95 MHz.[6] This supports our assignment above.

The NQR spectrum of II consists of two groups of lines. From a comparison of the spectrum of II with the spectra of III and I, it is evident that the two lines at about 38 MHz are assignable to the $=CCl_2$, and the other two lines at about 38.7 MHz, to the $>CCl_2$. Because of the conjugative effect, the frequency of an olefinic chlorine is somewhat lower than the frequency of a paraffinic chlorine.

The III molecule has two functional groups, $-CCl_3$ and $>CCl_2$. The three resonance lines at about 40.5 MHz were found to disappear gradually at about 210°K (the so-called "fade-out" phenomenon). This phenomenon has also occasionally been observed for compounds containing trichloromethyl groups, $-CCl_3$.[20,21] Therefore, the three lines at about 40.5 MHz are assignable to the $-CCl_3$, and the other two lines at about 39 MHz, to the $>CCl_2$.

At room temperature, Furusaki has investigated the crystal structure of IV and found that the symmetry of this molecule is C_2.[12] He also found that there were seven crystallographically-nonequivalent chlorine atoms in the unit cell, while, in our NQR study of IV, only four resonance lines were observed at room temperature. Since the frequencies of these four lines decrease monotonously with an increase in the temperature, this crystal seems to undergo no phase transition between 77°K and room temperature. Therefore, the experimental fact that seven resonance lines were observed at 77°K is consistent with this crystal structure. The NQR spectrum of IV consists of two groups: three lines appeared in the frequency region from 39.7 to 40.5 MHz, and four lines, in the region from 37.4 to 38.0 MHz. The higher three lines, ν_1, ν_2, and ν_3, were found to fade out at about 260°K; they are assigned to the $-CCl_3$.

The six resonance lines found for the V compound may be divided into two groups, four lines centered at about 38.2 MHz and two lines centered at about 36.9 and 37.3 MHz. Since this molecule has four olefinic chlorines adjacent to the double bonds in the cyclopentadiene ring and two chlorines in the $=CCl_2$ group, the four higher-frequency lines may be attributed to the olefinic chlorines adjacent to the five-membered ring, and the two lower-frequency lines, to the chlorines in the $=CCl_2$ group. This assignment requires some explanation. If the assignemnt mentioned above for V is correct, the resonance frequencies of the chlorines in the $=CCl_2$ of V are lowered by about 1 MHz below the frequencies of the chlorines in the $=CCl_2$ of I, II, and IV. The decrease in the resonance frequency may be due to the contribution of the following structure to the ground state of V.

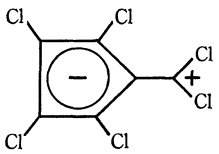

Fig. 3.

In this structure, the electrons of the p_π orbitals of chlorines in the $=CCl_2$ may be in part transferred to the adjacent carbon atoms. According to the theory of Townes and Dailey,[22,23] this decrease in the electron density of the p_π orbitals of chlorine atoms accounts for the decrease in the resonance frequency. Recently, Agranat *et al.* have suggested, in their study of dipole moments, a certain contribution of a dipolar structure to the ground state of V.[24] This supports the above

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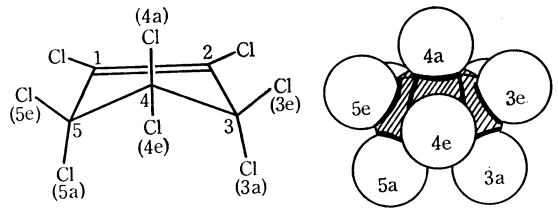
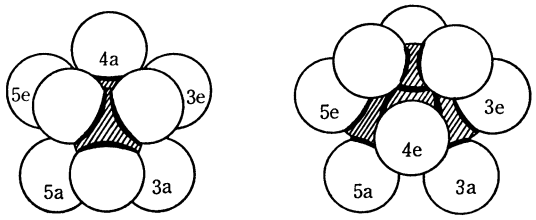


Fig. 4. Molecular model of perchlorocylcopentene, VI.

considerations.

In the NQR spectrum of VI, it is seen that one of the six frequencies of the geminal chlorines is considerably higher than the frequencies of the other geminal chlorines. This can be explained in terms of a strong electrostatic repulsion between the chlorine atoms. An examination of the molecular model of VI (Fig. 4) leads to the following results.

It can be seen in Fig. 4 that the distance between Cl (4e) and Cl(3a), and that between Cl(4e) and Cl(5a), are the shortest among those between the geminal chlorines. Thus, the equatorial chlorine, Cl(4e), is subject to a stronger electrostatic repulsion than any other geminal chlorine. The repulsive electrostatic interaction between chlorine atoms causes the migration of the electronic charge from the chlorine atoms to carbon atoms, and thus causes a diminution in the ionic character of the C–Cl bond. The decrease in the ionic character results in the shift of the resonance frequency to the higher-frequency side.[22,23] The highest frequency line, ν_1, of VI thus assignable to the equatorial chlorine, Cl (4e).



equatorial conformer axial conformer

Fig. 5. Two conformations of perchloro-(4-methylcyclopentene), VII.

The VII molecule has two possible conformations (Fig. 5). In either conformation, the degree of all the intramolecular Cl···Cl repulsive interactions may be larger than that in VI because of the extreme bulkiness of the $-CCl_3$ group. The ionic character of C–Cl bond in the $>CCl_2$ of VII is expected to be smaller than that of VI. This diminution of the ionic character accounts for the experimental fact that the average value of the resonance frequencies of VII shifts to a higher-frequency side compared to that of VI.

It should be noted that the average value of the resonance frequencies of the chlorines in carbon tetrachloride, CCl_4, is comparable to those of the chlorines in the $>CCl_2$ of VI and VII. According to the theory of Townes and Dailey,[22,23] the observed NQR frequency is related to the ionic and double-bond characters of the C–Cl bond and to the *s* character of the chlorine-bonding orbital. They also proposed that the amount of the *s* character was about 15% for the chlorine-bonding orbital in a C–Cl bond.[23] The double-bond character of the C–Cl bond in the $>CCl_2$ and CCl_4 may be neglected. Therefore, the ionic character of the C–Cl bond in the $>CCl_2$ of VI and VII is comparable to that of CCl_4.

Table 2. Resonance lines found to fade out and the temperatures, T_f, at which the resonance lines disappeared

No. of resonance lines	T_f (°K)
All lines of I	255
ν_1, ν_2, and ν_3 of III	210
ν_1, ν_2, and ν_3 of IV	260
All lines of V	255
ν_7 of VII	280

For several compounds, the fade-out phenomena were found at rather low temperatures. The temperatures, T_f, at which the resonance lines disappeared are summarized in Table 2. The fade-out of chlorine resonances has been reported for a number of compounds.[20,21,25,26] From the fact that the fade-out apparently occurs only in a solid where internal or molecular rotation is either definitely known to ocuur or is very likely to occur, it has been considered that such motions are responsible for the fade-out.[21] In the cases of III and IV, a similar mechanism may operate and the disappearance of the $-CCl_3$ chlorine resonances could results from the internal rotaion or rotational oscillation of the $-CCl_3$ group. This view is supported by the large X-ray temperature factors found for the chlorine and the carbon atoms in the $-CCl_3$ groups of IV.[12]

Furusaki, in his X-ray study of IV, has found close intermolecular Cl···Cl distances, 3.43, 3.56, and 3.58 Å for the $-CCl_3$ group.[12] Although the crystal structure of III has not yet been determined, the intramolecular Cl···Cl distances between the two $-CCl_3$ groups in this molecule are expected to be extremely short, for two bulky $-CCl_3$ groups are attached to either end of the C=C bond. However, the fade-out phenomena found for III and IV seem to suggest that the steric hindrance is not severe enough to prevent the internal rotation or rotational oscillation of the $-CCl_3$ group. Detailed studies of the mechanism of the fade-out phenomena found for I and V are now being undertaken by means of investigations of the crystal structures (at room temperature and at low temperatures), by thermal analysis (DTA and DSC), and by studying the temperature dependence of the dielectric constant and the electrical conductivity.

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