A Chlorine NQR Study of Trichloromethyl Derivatives. I

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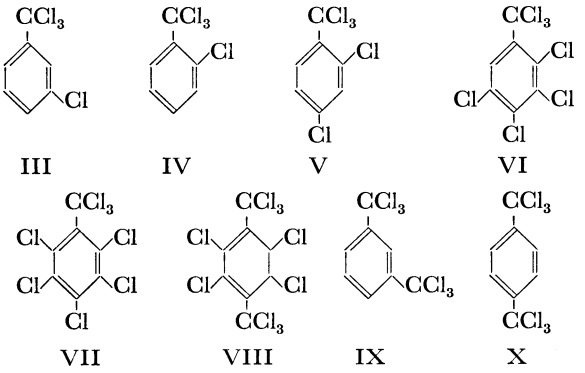
The chlorine NQR frequencies of several benzene derivatives with $-CCl_3$ groups were measured at temperatures above 77 K. For all the compounds studied, the NQR signals of the $-CCl_3$ groups were observed to fade out; the fade-out temperatures (T_f) were in the temperature range of 130—370 K. It was found that the most important factors involved in determining the T_f value are the intramolecular steric hindrance, hyperconjugation, and intermolecular interactions. In some compounds, an increase in the NQR frequency was found to be caused by the intramolecular steric hindrance.

It is well known that the chlorine NQR signals of the trichloromethyl ($-CCl_3$) group often fade out at temperatures far below the melting point. The fade-out temperatures (T_f) reported so far for several compounds are distributed over a fairly wide temperature range.[1-7] The object of this work is to explore the role of the various factors involved in determining the T_f value. For this purpose, several tens of compounds with $-CCl_3$ group(s) were investigated; of them, a series of benzene derivatives will be discussed here. Of the benzene derivatives, trichloromethylbenzene (I)[1,7] and 1-trichloromethyl-4-chlorobenzene (II)[5] have already been studied in detail. In this work, therefore, NQR measurements were carried out for the materials shown below.



III IV V VI

VII VIII IX X

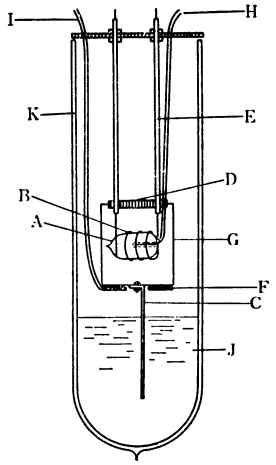


Fig. 1. Cryostat for the NQR measurement. A: Sample. B: Sample coil. C: Copper plate. D: Teflon. E: Transmission line (stainless steel pipe). F: Electric heater. G: Copper case. H: Thermocouple. I: Heater leads. J: Liquid nitrogen. K: Glass Dewar flask.

Experimental

The NQR signals of ^{35}Cl were detected by a LC-push-pull type superregenerative spectrometer.[8] For the measurement of the temperature dependence of the NQR frequency, the simple cryostat shown in Fig. 1 was employed. The temperature was controlled by changing both the amount of liquid nitrogen and the heater current. The temperature was measured with a calibrated copper-constantan thermocouple.

A commercial compound (Tokyo Kasei) of 1-trichloromethyl-3-chlorobenzene (III) was purified by vacuum distillation (3 Torr, 120 °C). Commercial reagents (Tokyo Kasei) of 1-trichloromethyl-2-chlorobenzene (IV), 1-trichloromethyl-2,4-dichlorobenzene (V), 1,3-bis(trichloromethyl)benzene (IX), and 1,4-bis(trichloromethyl)benzene (X) were purified by recrystallization from ethyl ether. The 1-trichloromethyl-2,3,4,5-tetrachlorobenzene (VI), 1-trichloromethyl-2,3,4,5,6-pentachlorobenzene (VII), and 1,4-bis(trichloromethyl)-2,3,5,6-tetrachlorobenzene (VIII) were supplied by Professor Akira Fujino, Osaka City University.

Results and Discussion

The ^{35}Cl NQR frequencies of III, IV, V, VI, VII, VIII, IX, and X were measured at temperatures above 77 K. The NQR frequencies of these compounds at 77 K are listed in Table 1. The results obtained for III, IV, IX, and X at 77 K in good agreement with the data reported by Ardalan and Lucken,[9] except for slight differences in the data for IV and IX (see footnotes of Table 1). The NQR signals corresponding to the chlorine atoms of the $-CCl_3$ group (α-chlorine atoms) of each compound were found to fade out at temperatures below the melting point of the compound. The fade-out temperatures (T_f) are summerized in Table 2, together with the melting points (T_m).

Four NQR lines were observed for V at 77 K. As judged by the value of the resonance frequency, two of them (39.733 and 39.405 MHz) are assigned to α-chlorine atoms, and, as the intensity of the line at 39.405 MHz is stronger than that at 39.733 MHz, the lower-frequency line is assigned to two equivalent α-chlorine atoms.

The NQR spectrum of VI consists of twelve lines. The number of resonance lines indicates that there are two crystallographically nonequivalent molecules in a unit cell and that each molecule has a mirror plane which coincides with the benzene ring. The most energetically favorable arrangement for the $-CCl_3$

Table 1. The ^{35}Cl NQR frequencies of some benzen derivatives with $-CCl_3$ group(s) at 77 K

Compound	Frequency/MHz			
III[a]	39.510	39.065	39.045	35.010*[b]
IV[c]	39.613	39.602	39.155	35.798*
V[d]	39.733	39.405	36.816*	35.296*
VI	40.093	39.909	39.851	39.709
	38.430*	38.071*	38.049*	37.990*
	37.907*	37.850*	37.588*	37.274*
VII	41.744	41.034	39.794	39.361*
	38.954*	38.878*	38.467*	38.377*
VIII	41.649	41.214	41.169	40.491
	39.689	39.381	39.204*	38.874*
	38.830*	38.825*		
IX[e]	39.492	39.470	39.097	38.993
	38.921	38.783	38.698	38.590
	38.472			
X[f]	39.628	39.408	39.343	39.322
	39.276	39.196	38.907	38.716
	38.300			

a) By thermal analysis, this compound was found to form a glassy state from a supercooled liquid (T_g=166 K and T_c=201 K). For a quenched specimen, no NQR signals were observed because of the formation of the glassy state. b) The NQR frequencies corresponding to chlorine atoms attached to the benzene ring are denoted by asterisks. c) Aldaran and Lucken (A & L) reported three frequencies, 39.602, 39.158, and 35.794 MHz, at 77 K and assigned the highest one to two equivalent α-chlorine atoms.[9] The existenec of the four lines was confirmed in this work by the temperature dependence of the NQR frequencies. d) Sasikala and Murty reported three NQR frequencies, 38.76, 36.40, and 34.87 MHz, at room temperature.[10] e) A & L reported twelve frequencies, 39.481, 39.461, 39.307, 39.084, 38.987, 38.913, 38.761, 38.692, 38.640, 38.570 38.462, and 38.440 MHz, at 77 K.[9] Nine of these frequencies agreed with the present data, but the rest of them (39.307, 38.640, and 38.440 MHz) were not detected, even in spite of careful measurement. f) By thermal analysis it was found that the room-temperature modification of X is transformed into a high temperature phase at 362 K. The frequencies given in this table correspond to the room-temperature modification. A supercooled high-temperature modification gave fairly broad NQR signals at 77 K, their frequencies being 39.54, 39.42, 39.34, 39.23, and 38.82 MHz.

groups in these molecules appears to be the one in which two α-chlorine atoms are located symmetrically above and below the plane of the benzene ring, while the third one lies on it, pointing away from the ortho chlorine atom. Therefore, the two crystallographically nonequivalent molecules have the same molecular configuration. Four of the twelve lines of VI (40.093, 39.909, 39.851, and 39.709 MHz at 77 K) were found to fade out; they are assigned to the two $-CCl_3$ groups of the two crystallographically nonequivalent molecules. Since the intensities of the signals at 40.093 and 39.851 MHz are approximately twice as strong as those at 39.909 and 39.709 MHz, each of the former two lines corresponds to two equivalent α-chlorine atoms in a molecule.

Table 2. Fade-out temperatures (T_f) of the NQR signals of $-CCl_3$ groups and melting points (T_m) of several benzene derivatives

Compound	T_f/K	T_m/K
I[a]	130 and 215	265
II[b]	250	270
III	260	270
IV	260	303
V	320	323
VI	330 and 370	395
VII	260	345
VIII	300	380
IX	145—160	308
X	160—170 and 255	383

a) Ref. 7. b) Ref. 5.

Three of the eight NQR lines of VII (41.744, 41.034, and 39.794 MHz) and six of the ten NQR lines of VIII (41.649, 41.214, 41.169, 40.491, 39.689, and 39.381 MHz) are undoubtedly to be assigned to α-chlorine atoms, because of the fade-out phenomena of these lines.

Ballester *et al.* pointed out that the $-CCl_3$ group of VII is arranged in such a way that two α-chlorine atoms lie on one side, and the third one on the other side, of the plane of the benzene ring, and that the benzene ring is distorted as the result of a strong steric repulsion between the α-chlorine atom and the ortho substituent.[11] As is shown in Table 1, the $-CCl_3$ group of VII gives three NQR lines, two of them with relatively high resonance frequencies (41.744 and 41.034 MHz) as compared to the third one (39.794 MHz). The two higher frequency lines are probably to be assigned to the two α-chlorine atoms, which interact with the ortho substituents. The reason for this assignment is as follows: the steric repulsion between the chlorine atoms causes a decrease in the ionic character of the C–Cl bond in the $-CCl_3$ group, and, according to the theory of Townes-Daily,[12] the decrease in the ionic character increases the resonance frequency.

For the chlorine atoms attached to the benzene ring (olefinic chlorine atoms) of VII, the mean NQR frequency is 38.80 MHz, while that of hexachlorobenzene is 38.45 MHz.[13] The rise in the NQR frequency in VII is also to be attributed to the steric repulsion between chlorine atoms. In the case of VIII, the mean NQR frequency (38.93 MHz) of the olefinic chlorine atom is higher than that of VII, in accord with the fact that, in VIII, all of the olefinic chlorine atoms are repelled.

The fade-out phenomenon of the NQR signals of the $-CCl_3$ group is known to be due to the reorientation of the group around its three-fold axis.[14] Recently, several authors have reported both the values of the potential barriers (V_0) for the reorientation of the group and the T_f's for some compounds.[1-3,5,6] These data show that the values of V_0 and T_f vary widely from compound to compound and that the T_f value tends to rise with an increase in the V_0 value. Of the benzene derivatives studied in this work, the substances with a

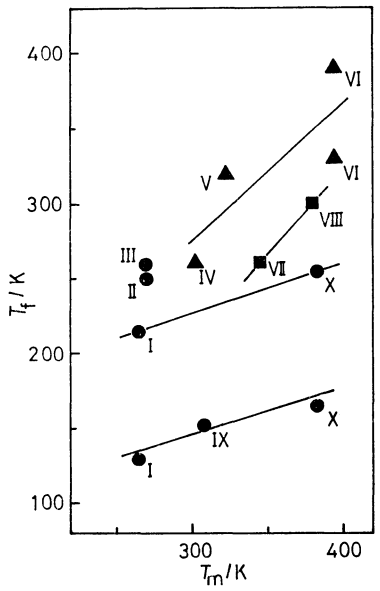


Fig. 2. Fade-out temperature (T_f) *vs.* melting point (T_m) plots of benzene derivatives.
●: Substances without ortho-substituent,
▲: substances with ortho-substituent(s),
■: perchloro-compounds.

$-CCl_3$ group with ortho substituent(s) show considerably high T_f values. Since the intramolecular steric hindrance between the $-CCl_3$ group and ortho substituent(s) raises a potential barrier for the reorientation of the $-CCl_3$ group, it seems reasonable that the substances with ortho substituent(s) show high T_f values. It is worth noting that the fade-out phenomenon was observed even for the $-CCl_3$ groups of VII and VIII, in which the groups are flanked by two ortho chlorine atoms. Moreover, despite the presence of the two ortho substituents, the T_f values of VII and VIII are comparable with those of other compounds with one ortho substituent. Therefore, the distortion of the benzene ring in VII and VIII relieves the steric hindrance, thus decreasing the value of V_0.

In the single-crystal NQR study of II, Kiichi *et al.* reported the presence of hyperconjugation between the $-CCl_3$ group and the π-systems of the benzene ring.[5] According to them, the hyperconjugation tends to lower both the NQR frequency and the magnitude of the temperature coefficient of the α-chlorine atom associated with the hyperconjugation. The $-CCl_3$ group of III gives the NQR frequencies of 39.510, 39.065, and 39.045 MHz at 77 K; their mean temperature coefficients are -3.00, -3.23, and -2.51 kHz/K respectively. The possibility of the hyperconjugation in III is suggested by the fact that the lowest frequency line exhibits the smallest absolute value of the temperature coefficient. In addition, the high T_f value of III seems to support the possibility of the hyperconjugation.[5,6]

Quite different T_f values were found for the $-CCl_3$ groups of the two crystallographically nonequivalent molecules of VI. Among the nine NQR signals of X, three signals (39.343, 39.276, and 38.716 MHz at 77 K) were observed up to 255 K, while the others faded out in the temperature region of 160—170 K. The large differences in T_f evidently indicate that, in each of these compounds, there exist two kinds of $-CCl_3$ groups with different potential barriers for the reorientation of the group. The cause of the difference in T_f for VI is probably of intermolecular nature, because the two crystallographically nonequivalent molecules have almost the same molecular configuration.

For the benzene derivatives studied, T_f *vs.* T_m plots are shown in Fig. 2. In the series of the substances without an ortho substituent (denoted by ● in Fig. 2), T_f tends to increase with an increase in T_m.[15] The same trend can be seen for the compounds with an ortho substituent (denoted by ▲) and also for the perchloro compounds (denoted by ■). Since T_m reflects the degree of intermolecular interaction, this tendency implies that T_f (in other words, V_0) is affected not only by intramolecular interactions, but also by intermolecular ones.

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