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A Chlorine NQR Study of *anti*-Perchloro-(3,4,7,8-tetramethylenetricyclo [4.2.0.0^{2,5}] octane), $C_{12}Cl_{12}$

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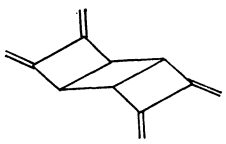
In our previous work, we investigated the correlations between the molecular structures and the NQR frequencies of perchloro-compounds, using seven perchloro-compounds for which the crystal or molecular structures have been well established.[1)]

In the present paper, in connection with the previous work, we wish to report on the NQR study of *anti*-perchloro-(3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]-octane) (I), for which the crystal and molecular structures have been determined.[2)] The details of the experimental procedures have also been reported previously.[1,3)]



I

The NQR frequencies were measured at temperatures in the range from 77 to 360°K. The experimental results at 77°K are given in Table 1. The intensities of these resonance lines were rather weak, and the half-widths were about 6.0±0.5 KHz at 77°K. The temperature dependence of these lines is shown in Fig. 1. Two lines, ν_2 and ν_3, were found to disappear at about 273 and 225°K respectively (fade-out). Figure 1 shows that the resonance frequencies of the other four lines decrease monotonously with an increase in the temperature. This suggests that I undergoes no phase transition between 77°K and room temperature. Therefore, six crystallographically-nonequivalent chlorine atoms exist in the unit cell of the crystal of I at room temperature, although only four resonance lines were observable at room temperature. Furusaki, in his X-ray study of I at room temperature, assumed that the space group was $P\bar{1}$.[2)] Our NQR results are consistent with his assumption.

From a structural point of view, I is related to perchloro-(3,4-dimethylenecyclobutene) (II) and perchloro-(1,2-dimethylenecyclobutane) (III). Their

Table 1. The nuclear quadrupole resonance frequencies of ^{35}Cl of I and the relative intensities of the resonance lines at liquid nitrogen temperature

No.	Resonance frequency (MHz)	Relative intensity
ν_1	38.070 (30.003)[a)]	9
ν_2	37.862 (29.839)	7
ν_3	37.784 (29.779)	10
ν_4	37.555 (29.598)	10
ν_5	37.541 (29.587)	9
ν_6	37.101 (29.239)	8

a) The value in ( ) is the frequency of ^{37}Cl.

1) M. Hashimoto and K. Mano, This Bulletin, **45**, 706, (1972).
2) A. Furusaki, *ibid.*, **40**, 758 (1967).
3) K. Mano, K. Kusuda, A. Fujino, and T. Sakan, *Tetrahedron Lett.*, **1966**, 489.

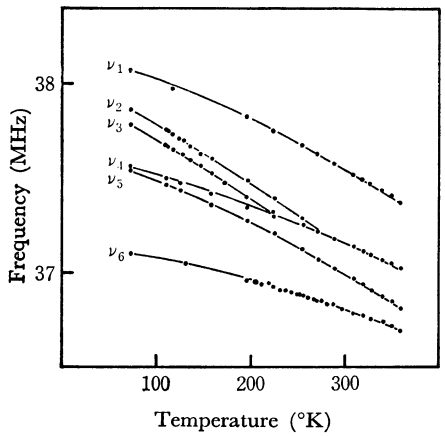


Fig. 1. Temperature dependence of the NQR frequencies of I.

NQR spectra, discussed in the previous paper, are of assistance in assigning the resonance lines of I.

II III

The NQR frequencies of ^{35}Cl in the dichloromethylene groups of II and III lie in a frequency region from about 37.8 to 38.1 MHz at 77°K.[1] Among the six lines of I, therefore, the five lines besides ν_6 are assignable to the chlorine atoms in the dichloromethylene groups on the basis of a comparison with the data for II and III.

The chlorine atoms corresponding to ν_2 and ν_3 may have large temperature factors, because the fade-out found for the two lines may be due to the reorientation of the chlorine atoms. In fact, according to the X-ray study of I,[2] two of the chlorine atoms, Cl(4) and Cl(5)

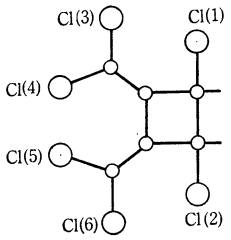


Fig. 2. One half of the molecule of I.

in Fig. 2, have unusually large temperature factors. Therefore, ν_2 and ν_3 are assignable to Cl(4) and Cl(5). For several other compounds, a correlation between the fade-out and the large temperature factor has also been found.[1,4]

Although the symmetry of I is C_i, the molecular geometry shows that Cl(1) is nearly equivalent to Cl(2).[2] Consequently, the characteristics of the torsional vibrations may be almost the same for these two chlorine atoms. This means that the temperature coefficient of the resonance frequency of Cl(1) is also similar to that of Cl(2).[5] For a similar reason, the temperature coefficients of the resonance frequencies of Cl(3) and Cl(6), and those of Cl(4) and Cl(5), may be almost the same. Figure 1 shows, on the basis of a comparison of the temperature dependence of the resonance frequency, that the six lines of I can be divided into three pairs of lines, ν_1 and ν_5, ν_2 and ν_3, and ν_4 and ν_6. As has been described above, the second pair, ν_2 and ν_3, are assignable to Cl(4) and Cl(5). The first pair, ν_1 and ν_5, may be assigned to Cl(3) and Cl(6), and the third, to Cl(1) and Cl(2).

4) M. T. Rogers and J. A. Ryan, *J. Phys. Chem.*, **72**, 1340 (1968).

5) H. Bayer, *Z. Phys.*, **130**, 227 (1951).