^{35}Cl-NQR of Some Chlorocarbons and Oxochlorocarbons with a Small Ring[†]

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^{35}Cl-NQR of two chlorocarbons and six oxochlorocarbons, all having a small ring, were measured in the temperature range 77—300 K. The NQR line groups for the allylic and vinylic chlorine atoms appear separately in the five-membered ring compounds, whereas they are concentrated in a rather narrow region near 38 MHz in the four-membered ones. Perchlorocyclopropene possesses at least three crystal modifications at 77 K, the most stable one of which has only two lines in the temperature range examined. The line assignments, and the hyperconjugative effect in some of them, are discussed with reference to the CNDO/2 MO calculation data.

By means of ^{35}Cl-NQR we can discuss the hyperconjugative effects in the ground state of an organic molecule. Unexpected lowering of the observed frequencies in chlorofluoromethanes, chloromethyl ethers,[1,2] and benzyl chlorides[3] was explained by the interaction between the C–Cl σ bond and the p-orbital of the adjacent first-row substituents. Considering the fitness of chlorocarbons (no hydrogen bond in or between the molecule(s)) for the purpose, we examined the ^{35}Cl-NQR of some cyclic chloro- and oxochlorocarbons in which all the chlorine atoms on the ring carbons have a rigid conformation. We found that in some of them the hyperconjugative effect causes a significant frequency shift from the expected value.

Experimental

Except for commercial perchlorocyclopropene, all the specimens were prepared according to the methods described.[4–8] They were purified by monitoring their IR spectra and elemental analyses. Melting points are: perchloro-4-cyclopentene-1,3-dione (**1**), 68 °C; perchloro-2-cyclopentenone (**2**), 28 °C; perchloro-3-cyclopentenone (**3**), 89 °C, perchloro-3,4-dimethylenecyclobutane-1,2-dione (**4**), 167 °C; perchloro-2,3-dimethylenecyclobutanone (**5**), 68 °C; perchloro-2-cyclobutenone (**6**), −1 °C (by DSC); perchlorocyclobutene (**7**), 50 °C.

A Decca Radar NQR Spectrometer and a superregenerative spectrometer were used. Temperature dependence of the NQR signals was measured by Hashimoto's method.[9] Resonance frequency values obtained by extrapolating the observed variation to 0 K were taken for minimizing the thermal effect of the crystalline lattice on frequencies.

Results and Discussion

The resonance frequencies of six oxochlorocarbons (**1**—**6**) and two chlorocarbons (**7** and **8**) at several temperatures are given in Table 1. The stick diagram (Fig. 1) shows the values at 0 K together with those of the related compounds, perchlorocyclopentene (**9**) and perchloro-1,2-dimethylenecyclobutane (**10**).

Five-membered Ring Compounds. The resonance lines of all oxo compounds as well as the reference chlorocarbon **9** fall into two clearly separated frequency regions, one lower than 38.1 MHz, and the other above 39.1 MHz. The lower group corresponds to the vinylic (v-), and the higher to the allylic (a-) chlorine substituents. The numbers of observed lines for **1** and **3** were two and three, respectively, indicating that the former molecule has a C_2 and/or two C_s, and the latter a C_2 or C_s symmetry element(s) in their crystals.

TABLE 1. TEMPERATURE DEPENDENCES OF NQR LINES IN SOME CHLOROCARBONS AT SEVERAL TEMPERATURES

		77 K	195 K	288 K	0 K[a)]
1	ν_1	39.848	39.272	38.765	40.07
	ν_2	36.573[b)]	36.105	35.692	36.72
2	ν_1	40.362	40.060	39.749	40.45
	ν_2	40.157	39.789	39.429	40.30
	ν_3	39.333	39.077	38.810	39.38
	ν_4	39.178	38.905	38.632	39.28
	ν_5	38.014	37.684	37.381	38.14
	ν_6	37.266	36.905	36.587	37.39
3	ν_1	39.414	38.921	38.403	39.55
	ν_2	39.082	38.577	38.036	39.22
	ν_3	37.674	37.376	36.997	37.75
4	ν_1	37.948	37.372	37.508	38.02
	ν_2	37.389	37.115	36.836	37.45
5	ν_1	38.304	37.874[c)]	37.447	38.40
	ν_2	37.921	37.465[c)]	37.006	38.01
	ν_3	37.798	37.494[c)]	37.190	37.86
	ν_4	37.723	37.425[c)]	37.104	37.80
	ν_5	37.562	37.153[c)]	36.701	37.64
	ν_6	37.562	37.254[c)]	36.950	37.62
6	ν_1	37.780[b)]	37.461	37.420[d)]	37.90
	ν_2	37.645[b)]	37.354	37.319[d)]	37.75
	ν_3	37.296[b)]	36.971	36.940[d)]	37.42
	ν_4	36.707[b)]	36.371	36.337[d)]	36·82
7	ν_1	38.482	38.151	37.789	38.55
	ν_2	38.412[b)]	38.037	37.637	38.50
	ν_3	38.352[b)]	38.011	37.637	38.42
	ν_4	38.230[b)]	37.843	37.439	38.34
	ν_5	36.647[b)]	36.259	35.843	36.74
	ν_6	36.480[b)]	36.105	35.711	36.57
8	ν_1	38.730	38.308	38.144[e)]	38.80
	ν_2	36.471	36.131	35.933[e)]	36.54

a) Extrapolated values. b) *Cf.* C. Brevard and J. M. Lehn, *J. Chim. Phys. Physicochim. Biol.*, **1968**, 727. Their ν_2 value for **1** differs exactly 1000 kHz from ours. However, their values for **6** and **7** and those we obatined are in good agreement. c) At 200 K. d) At 206 K. e) At 233 K.

The lowest line ν_6 in **2** is easily assigned to a v-Cl, β-positioned to the carbonyl group. The two-paired a-Cl's resonate in sufficiently separated regions, re-

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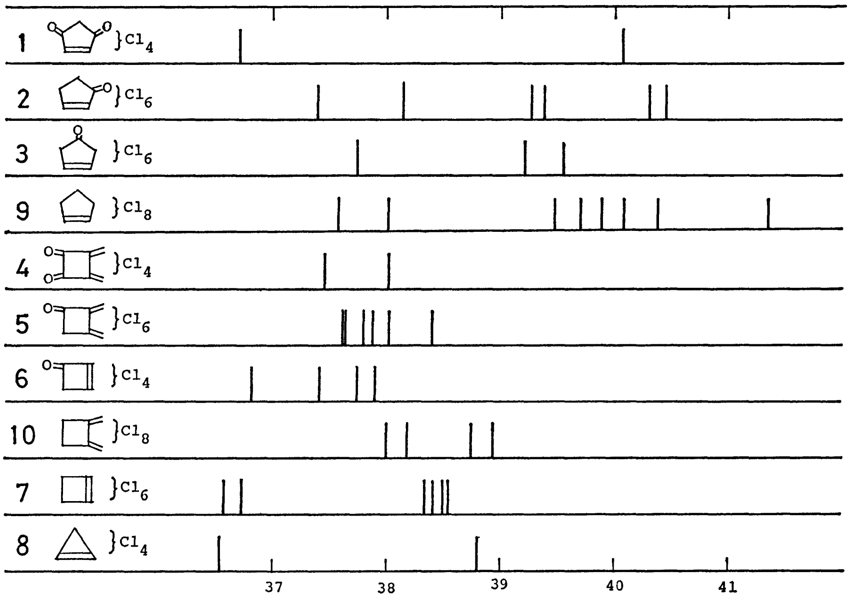


Fig. 1. Resonance lines obtained by extrapolating the thermal variation to 0 K.

spectively *ca.* 39.3 and 40.4 MHz. The highest two among them can be explained in terms of the hyperconjugative interaction between the C_5–Cl bond and the carbonyl group which unusually decreases the ionicity of the allylic chlorine (the term "allylic" is also applied to the chlorine atom α-positioned to the carbonyl group). The remaining pairing lines, ν_3 and ν_4, can be assigned to the *a*-Cl's at C_4.

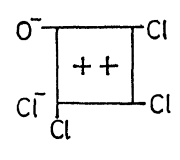
The *a*-Cl (ν_1) in **1** appears in a region similar to the highest one in **2**. In this case, we see no additive effect of hyperconjugation due to the second carbonyl group.

The frequency of *v*-Cl in **3** is situated roughly at an average of the highest two lines for **9**. The *a*-Cl's resonate in the same frequency region as do the *a*-Cl's at C_4 in **2**. Thus, the carbonyl seems to have no influence on all the resonance frequencies.

Four-membered Ring Compounds. In contrast to the above, all the NQR lines of oxochlorocarbons **4**—**6** were observed in a narrow range near 38 MHz. Dioxo compound **4** gave two lines which suggest a C_2 and/or a C_s symmetry in the crystal, its splitting (*ca.* 600 kHz) due to inner and outer *v*-Cl's being appreciably larger than the corresponding one in chlorocarbon **10**. The large splitting suggests a difference in contribution of each carbonyl group to the conjugation with chlorine atoms between the inner *v*-Cl and the outer one. Preliminary MO calculation data (CNDO/2)[11] indicate that the lower line corresponds to the inner substituent.

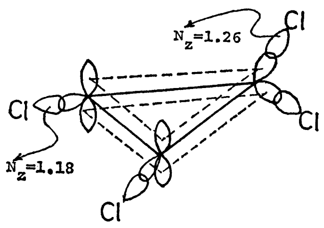
Mono oxo compound **5** has five lines at 77 K. However, temperature dependence observation of these lines revealed that **5** has essentially six lines in the range 77—310 K; three (ν_1, ν_2, and ν_3) of them having a steeper temperature gradient, *ca.* 4.2 kHz/K, and the rest having *ca.* 2.9 kHz/K. All the lines appear in the *v*-Cl region after 0 K extrapolation, suggesting that the hyperconjugation with C=C double bond would be dominant over that with the C=O group. Reflecting this situation, the calculation gave an appreciably large N_z (1.233, AO population of p_z) of the *a*-Cl. Such a polarization in the Cl at C_4 is due to the contribution of a stabilized allylic cation with full π-conjugation. It was difficult to assign the six lines because of their concentration in a narrow range within crystal field effects. However, the calculated line pattern for **5** with a twisted geometry of $C=Cl_2$ groups resembles the observed one.[11,12]

Compound **6**, having four NQR lines all in the *v*-Cl region (below 38.0 MHz), shows an almost simultaneous fade-out at around 210 K, which seems to be related to the phase transition at 220 K evidenced by DSC analysis. The extraordinary low values for the *a*-Cl's suggest the contribution, in the ground state, of some stabilized structure, perhaps an aromatized one as shown below, rather than a hyperconjugated. In a compound like **7**, where no similar contribution can be expected, six lines appear in two groups well separated.



Three-membered Ring Compound. Perchlorocyclopropene **8** is an interesting compound in view of NQR spectra. Lucken and Mazeline reported six lines at 77 K, falling into two frequency groups (four: 38.2—38.8; two: 36.4—36.8 MHz).[13] They assigned the higher line group to *a*-, and the lower to *v*-Cl's. Smith and West later gave a completely inversed assignment on the basis of the data for some chlorocyclopropene derivatives.[14] We found from both NQR and DSC studies that **8** possesses at least three crystal modifications at 77 K. The most stable form, obtained by annealing **8** at Dry Ice temperature for 72 h, has only two NQR lines with very strong intensities in the temperature range 77—233 K (mp). Thus, it should have a C_2 and/or two C_s symmetry in the crystal.

Prediction from MO calculation strongly supports West's assignment.[14] The inversion of the frequency region between *a*- and *v*-Cl is attributed to both an extraordinary increase in N_z of the *a*-Cl (1.261) and a decrease in that of *v*-Cl (1.181).[11] The former is caused by the hyperconjugation with the C=C bond which stabilizes its cyclopropenium cationic structure in the ground state of the molecule.



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