Microwave Spectrum, Structure, and Quadrupole Coupling Constant of *o*-Chlorophenol

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The microwave spectrum of *o*-chlorophenol has been observed in the frequency range 10—34 GHz. The rotational and centrifugal distortion constants were obtained for two isotopic species, $^{35}ClC_6H_4OH$ and $^{37}ClC_6H_4OH$. The analysis of the hyperfine structure gives the following nuclear quadrupole coupling constants for ^{35}Cl species: $\chi_{aa}=-67.6$, $\chi_{bb}=33.3$, and $\chi_{cc}=34.3$ (MHz). The spectrum assigned has been attributed to the *cis*-form (intramolecularly hydrogen bonded between Cl and HO) from a brief consideration of the relative intensity of the a- and b- type transitions. No significant effect of the intramolecular hydrogen bonding on the nuclear quadrupole coupling was observed.

Many studies on the molecular structure of *o*-chlorophenol, mainly by means of infrared spectroscopy, have been reported by a number of authors in the last four decades.[1,2] According to these studies, *o*-chlorophenol exists as a mixture of two isomers, the *cis*- and *trans*-forms, in the gas and liquid phases and in solutions (the *trans*-form is the conformer with the hydroxyl hydrogen pointed away from the chlorine, and the *cis*-form with the hydroxyl hydrogen pointed toward to the chlorine), and the *cis*-form is known to form intramolecular hydrogen bonding between the chlorine atom and the hydroxyl group. Carlson *et al.*[2] estimated the population of the *trans*-form as 6.5% at room temperature from the analysis of the torsional frequencies of the hydroxyl group and concluded that the *cis*-form was more stable than the *trans*-form in the gas phase. Two benzene derivatives which have the intramolecular hydrogen bonding have so far been studied by the microwave spectroscopy: salicylaldehyde[3] and *o*-nitrophenol.[4] It is interesting to study the structure of the *o*-chlorophenol molecule in the gas phase by means of microwave spectroscopy, because this molecule is one of those which have the possibility of forming the intramolecular hydrogen bonding.

Azrak and Wilson[5] studied in detail the influence of the hydrogen bonding on the quadrupole coupling constants for 2-chloroethanol, but they observed no significant effect.

The purposes of the present investigation of *o*-chlorophenol are to find out whether the dominant conformation is *cis*- or *trans*-form in the gas phase and to what extent the nuclear quadrupole coupling constants of chlorine are affected by the intramolecular hydrogen bonding in the *cis*-form.

Experimental

The sample used was obtained commercially and was distilled *in vacuo*. The purity of the sample was checked through its NMR and IR spectra. The microwave spectrum was measured with a conventional spectrometer in the frequency range of 10—34 GHz. A square wave of 100 kHz was used for the Stark modulation. Measurements were made at room temperature with sample pressures of 1.3—5.3 Pa. The absorption lines were displayed on a recorder. Frequency measurements were made with a Hewlett-Packard 5245L electronic counter. The accuracy of the measured frequency was better than 0.2 MHz for most lines and it was better than 0.5 MHz for the broadened lines and for the lines which had a strong line nearby.

Results and Discussion

Analysis of the Spectrum. The observed spectrum consisted of very many lines in the observed region. This complexity of the spectrum comes from the existence of two chlorine isotopic species in the vibrational ground state as well as in their low frequency vibrational excited states. A molecular model of a planar structure was constructed from the structural parameters of chlorobenzenes[6] and phenols.[8] The model calculation for either *cis*- or *trans*-form, where the Ray's asymmetry parameters for both are $\kappa\approx-0.46$, indicated that the transitions of the a- and b-types will appear in the observed frequency region. The initial step of the assignment was for both a- and b-type R-branch transitions. Clear quartets were observed for $J=9\leftarrow8$, $10\leftarrow9$, and $11\leftarrow10$ transitions with $K_{-1}=0$ and 1, and the separations between the two inner lines of the quartets were 12, 5, and 2 MHz, respectively. The assignments were confirmed by comparing the observed hyperfine structures with the predicted ones for the b-type Q-branch transitions with high-J values. The prediction was made using the nuclear quadrupole coupling constants of chlorobenzene[6] and with the planar molecular models of the *cis*- and *trans*- forms.

Many transitions were observed as doublets with separations of a few MHz due to the nuclear quadrupole coupling of chlorine. The center of the doublet was taken as the unperturbed frequency and was used for the least-squares fitting to obtain the rotational and centrifugal distortion constants. The assigned transitions are given in Tables 1 and 2 for both $^{35}ClC_6H_4OH$ and $^{37}ClC_6H_4OH$ species. The spectrum of $^{35}ClC_6H_4OH$ was fitted by the following seven variables: the three rotational and the four centrifugal distortion constants. For the $^{37}ClC_6H_4OH$ species, only six parameters (three rotational and three centrifugal distortion constants) were obtained because only a small number of high-J transitions were observed and the *hfs* were not well resolved. Table 3 gives the parameters thus obtained. The errors attached are the standard deviations obtained from the least-squares fits. The magnitudes of the centrifugal distortion constants τ obtained were small, as expected from several aromatic molecules.[7]

Table 1. Observed frequencies of R-branch transitions (MHz)

Transition	o-$^{35}ClC_6H_4OH$		o-$^{37}ClC_6H_4OH$	
	Observed	$\Delta\nu$ a)	Observed	$\Delta\nu$ a)
$8_{0,8}-7_{1,7}$	17329.85	−0.06		
$8_{1,8}-7_{1,7}$	17339.42	0.01		
$8_{0,8}-7_{0,7}$	17354.38	0.09		
$8_{1,8}-7_{0,7}$	17363.93	0.13		
$9_{0,9}-8_{1,8}$	19379.76	0.07	19035.22	−0.03
$9_{1,9}-8_{1,8}$	19383.31	0.00	19039.73	−0.21
$9_{0,9}-8_{0,8}$	19389.28	0.08	19047.11	−0.09
$9_{1,9}-8_{0,8}$	19392.80	−0.01	19051.91	0.03
$10_{0,10}-9_{1,9}$	21423.55	0.03	21044.14	0.21
$10_{1,10}-9_{1,9}$	21424.87	0.01	21046.09	0.36
$10_{0,10}-9_{0,9}$	21427.13	−0.00	21048.46	−0.15
$10_{1,10}-9_{0,9}$	21428.57	0.10	21050.53	0.11
$9_{1,8}-8_{2,7}$	21250.81	0.33		
$9_{2,8}-8_{2,7}$	21381.35	−0.02		
$9_{1,8}-8_{1,7}$	21539.16	−0.10		
$9_{2,8}-8_{1,7}$	21670.09	−0.06		
$11_{0,11}-10_{1,10}$	23465.10	0.09	23049.85	0.10
$11_{1,11}-10_{1,10}$	23465.54	0.04	23050.57	0.14
$11_{0,11}-10_{0,10}$	23466.40	0.04	23051.71	0.16
$11_{1,11}-10_{0,10}$	23466.97	0.12	23052.31	0.08
$10_{1,9}-9_{2,8}$	23397.50	0.24		
$10_{2,9}-9_{2,8}$	23453.77	−0.04		
$10_{1,9}-9_{1,8}$	23527.95	−0.21		
$10_{2,9}-9_{1,8}$	23584.59	−0.11		
$12_{0,12}-11_{1,11}$	25505.89	0.25	25054.54	0.07
$12_{1,12}-11_{1,11}$	25505.89	0.07	25054.54	−0.18
$12_{0,12}-11_{0,11}$	25505.89	−0.24	25055.11	−0.04
$12_{1,12}-11_{0,11}$	25505.89	−0.42	25055.11	−0.29
$13_{0,13}-12_{1,12}$	27546.00	0.02	27058.66	−0.12
$13_{1,13}-12_{1,12}$	27546.00	−0.04	27058.66	−0.21
$13_{0,13}-12_{0,12}$	27546.00	−0.15	27058.66	−0.37
$13_{1,13}-12_{0,12}$	27546.00	−0.22	27058.66	−0.47
$14_{0,14}-13_{1,13}$	29586.25	0.03	29063.02	0.06
$14_{1,14}-13_{1,13}$	29586.25	0.01	29063.02	0.02
$14_{0,14}-13_{0,13}$	29586.25	−0.03	29063.02	−0.04
$14_{1,14}-13_{0,13}$	29586.25	−0.05	29063.02	−0.07
$15_{0,15}-14_{1,14}$	31626.47	0.03	31067.16	0.05
$15_{1,15}-14_{1,14}$	31626.47	0.03	31067.16	0.04
$15_{0,15}-14_{0,14}$	31626.47	0.01	31067.16	0.02
$15_{1,15}-14_{0,14}$	31626.47	0.00	31067.16	0.01
$16_{0,16}-15_{1,15}$	33666.68	0.03	33071.47	0.22
$16_{1,16}-15_{1,15}$	33666.68	0.02	33071.47	0.22
$16_{0,16}-15_{0,15}$	33666.68	0.02	33071.47	0.21
$16_{1,16}-15_{0,15}$	33666.68	0.02	33071.47	0.21

a) $\Delta\nu=\nu_{\text{obsd}}-\nu_{\text{calcd}}$.

Table 2. Observed frequencies of Q-branch transitions (MHz)

Transition	o-$^{35}ClC_6H_4OH$		o-$^{37}ClC_6H_4OH$	
	Observed	$\Delta\nu$ a)	Observed	$\Delta\nu$ a)
$22_{7,15}-22_{6,16}$	20473.57	0.05		
$23_{7,16}-23_{6,17}$	23759.24	0.08	22101.71	0.17
$17_{8,9}-17_{7,10}$	21300.12	0.30		
$18_{8,10}-18_{7,11}$	19727.84	0.14		
$19_{8,11}-19_{7,12}$	18012.45	−0.00	19087.63	0.04
$20_{8,12}-20_{7,13}$	16549.19	−0.02	17467.32	0.00
$21_{8,13}-21_{7,14}$	15773.54	−0.03	16301.36	0.05
$22_{8,14}-22_{7,15}$	16004.27	0.05		
$23_{8,15}-23_{7,16}$	17368.53	0.05	16664.15	0.05
$24_{8,16}-24_{7,17}$	19775.88	−0.12	18448.38	0.02
$25_{8,17}-25_{7,18}$	22918.62	0.06	21141.52	−0.01
$15_{8,8}-15_{7,9}$	23877.24	−0.36	24294.01	−0.38
$16_{8,9}-16_{7,10}$	23622.19	−0.14	24029.53	−0.08
$17_{8,10}-17_{7,11}$	23449.88	−0.11	23818.53	0.01
$18_{8,11}-18_{7,12}$	23436.71	−0.02	23727.29	0.00
$19_{8,12}-19_{7,13}$	23661.39	0.01	23830.32	0.14
$20_{8,13}-20_{7,14}$	24189.20	0.00	24195.98	0.00
$19_{9,10}-19_{8,11}$	24912.29	0.00		
$20_{9,11}-20_{8,12}$	23475.68	0.09	24570.23	−0.03
$21_{9,12}-21_{8,13}$	21689.74	−0.01	22971.35	−0.20
$22_{9,13}-22_{8,14}$	19810.38	−0.07	21125.06	−0.06
$23_{9,14}-23_{8,15}$	18270.08	−0.04	19359.16	−0.16
$24_{9,15}-24_{8,16}$	17518.30	−0.00	18108.21	0.03
$25_{9,16}-25_{8,17}$	17865.68	−0.03	17754.04	0.11
$26_{9,17}-26_{8,18}$	19414.25	0.04	18517.38	0.06
$27_{9,18}-27_{8,19}$	22032.67	0.08	20417.99	0.00
$28_{9,19}-28_{8,20}$	25369.39	0.13	23259.18	−0.28
$24_{10,14}-24_{9,15}$	23565.60	0.07	25127.58	0.05
$25_{10,15}-25_{9,16}$	21541.67	0.09	23107.64	−0.12
$26_{10,16}-26_{9,17}$	19947.93	−0.02	21207.67	0.09
$27_{10,17}-27_{9,18}$	19243.65	−0.05	19882.63	0.05
$28_{10,18}-28_{9,19}$	19727.06	−0.08	19525.32	−0.02
$29_{10,19}-29_{9,20}$	21471.47	−0.04	20354.47	−0.02
$30_{10,20}-30_{9,21}$	24302.80	−0.10	22374.73	0.27
$28_{11,17}-28_{10,18}$	23215.10	−0.03	25041.91	−0.06
$29_{11,18}-29_{10,19}$	21591.15	0.06	23017.48	0.05
$30_{11,19}-30_{10,20}$	20956.58	0.08	21628.78	−0.04
$31_{11,20}-31_{10,21}$	21593.98	0.06	21277.37	−0.12
$32_{11,21}-32_{10,22}$	23544.00	−0.09	22178.43	−0.17
$32_{12,20}-32_{11,21}$	23206.81	0.03	24793.15	0.02
$33_{12,21}-33_{11,22}$	22662.87	−0.18	23350.44	0.08
$34_{12,22}-34_{11,23}$	23470.61	0.01	23013.35	0.15
$35_{13,22}-35_{12,23}$	24801.26	−0.10		
$36_{13,23}-36_{12,24}$	24368.65	0.10	25050.05	−0.04

a) $\Delta\nu=\nu_{\text{obsd}}-\nu_{\text{calcd}}$.

This spectrum is assigned to the *cis*-form as described in the later sections. A search for lines arising from the *trans*-form has failed, probably because their intensities are weaker than those of the vibrational excited states of the *cis*-form.

Molecular Structure. A small value of the inertia defect, as given in Table 3, is a strong indication of the planar configuration of this molecule. The positive inertia defect indicates that the effect of the out-of-plane vibrational motion, probably the hydroxyl group torsion, is not dominant. This is in contrast to the small negative value for phenol (−0.03 amu Å^2).[8] The value for *o*-chlorophenol is comparable to that for chlorobenzene and therefore the vibrational amplitude of the OH-torsion is considered to be smaller than for phenol. This reflects that the OH group in

TABLE 3. ROTATIONAL CONSTANTS (MHz), CENTRIFUGAL DISTORTION CONSTANTS (kHz), AND INERTIA DEFECT (amu Å^2) OF o-CHLOROPHENOL

	$^{35}ClC_6H_4OH$	$^{37}ClC_6H_4OH$
A	2985.454±0.008	2976.812±0.011
B	1549.861±0.003	1510.810±0.004
C	1020.195±0.002	1002.147±0.001
τ_{aaaa}	−1.9 ±0.3	−1.7 ±0.3
τ_{bbbb}	−0.36 ±0.04	−0.29 ±0.03
τ_{aabb}	−0.1 ±0.2	0.0[a)]
τ_{abab}	−0.48 ±0.07	−0.50 ±0.02
$I_c-I_a-I_b$	0.014±0.002	0.015±0.002
N[b)]	88	67
σ[c)]	0.014	0.019

a) Assumed. b) Number of transitions used for the least-squares fitting. c) Standard deviation (MHz) of lines fitted.

TABLE 4. PRINCIPAL AXIS COORDINATES OF Cl (Å)[a)]

	$\lvert a\rvert$	$\lvert b\rvert$
Observed	2.0671±0.0001	0.5132±0.0004
Predicted		
cis model	2.042	0.566
trans model	2.086	0.504

a) $\lvert c\rvert=0$ assumed.

o-chlorophenol is more restricted in the molecular plane than in phenol, suggesting that the molecule is of the *cis*-form, having an intramolecular hydrogen bond between the hydroxyl group and the chlorine atom.

Kraitchman's equation was used to calculate the chlorine atom coordinates in the planar structure. The values obtained using the rotational constants A and B for both species are given in Table 4. The error limits given came from the errors in the moment of inertia. The predicted coordinates of the chlorine atom, with the regular hexagonal benzene ring, are included in Table 4. Comparing these results with the coordinates in the model structures, one cannot decide whether the set of coordinates determined corresponds to the *cis* or *trans* conformation.

To solve the problem of the conformation the relative intensity of the a- and b-type transitions was considered. Each of the lines of a quartet, consisting of the transitions $9_{0,9}\leftarrow 8_{1,8}$, $9_{1,9}\leftarrow 8_{1,8}$, $9_{0,9}\leftarrow 8_{0,8}$, and $9_{1,9}\leftarrow 8_{0,8}$, was observed with comparable intensities. The predicted line strengths of these a- and b-type transitions are almost the same for both of the conformations because they have almost the same asymmetric parameter, $\kappa\approx -0.46$. From the vector sum of the values for chlorobenzene[6)] and phenol[8)] the components of the electric dipole moment were predicted as given in Table 5. The ambiguity of the calculated intensity comes solely from the model structure and the interaction between two group moments, μ_{C-Cl} and μ_{OH}, but the distinction between *cis*- and *trans*-forms is clear. For the *cis*-form the intensities for the a- and b-type transitions should be almost the same, while for the *trans*-form the intensity for the a-type transitions should be larger than for the b-type transitions. Other similar sets of transitions: $J_{0,J}\leftarrow J-1_{1,J-1}$, $J_{1,J}\leftarrow J-1_{1,J-1}$, $J_{0,J}\leftarrow J-1_{0,J-1}$, and $J_{1,J}\leftarrow J-1_{0,J-1}$, with $J=10$ and 11 for ^{35}Cl and ^{37}Cl species, were also observed with comparable intensities. These results imply that the assigned spectrum came from the molecule which has a dipole moment with comparable magnitudes of the a- and b-components: the *cis* form.

TABLE 5. PREDICTED DIPOLE MOMENTS (debye)[a)]

	cis form	*trans* form
μ_a[b)]	1.2	2.3
μ_b	1.2	1.2

a) Calculated from the following values: $\mu_a=1.782$ for chlorobenzene[6)] and $\mu_a=0.13$ and $\mu_b=1.27$ for phenol.[8)] b) a- and b-axes refer to model structure.

Assuming the rigid planar structure, only two moments of inertia are independent. From the results for the two isotopic species, four structural parameters can therefore be determined, while other parameters are assumed. The parameters derived for the *cis*-form were the bond lengths C–Cl and C–O and the angles ∠C(2)–O–H and ∠C(1)–C(2)–O. Assumptions for the other parameters were as follows: the benzene skeleton is regular hexagonal and the C–C bond length is 1.399 Å; all the C–H bonds and the C–Cl bond are located on the ∠C–C–C bisectors; the C–H bond length is 1.084 Å and the O–H bond length is 1.040 Å. A plausible set of parameters obtained on these assumptions is shown in Table 6. The calculated moments of inertia using these parameters coincide with the observed values within 0.1 amu Å^2. For the distorted benzene skeleton, which is the same as for chlorobenzene,[9)] the parameters given in Table 6 were obtained. From two different assumptions about the skeleton structure, the same magnitudes of the C–Cl bond length as in chlorobenzene, and the same angle ∠C–C–O, extended by 2° from 120°, have been obtained.

Quadrupole Coupling Constants. The apparent splitting in the doublet was measured for high-J b-type Q-branch transitions as listed in Table 7. The hyperfine patterns were analyzed based on the first-order quadrupole correction computation using the

TABLE 6. STRUCTURAL PARAMETERS

	r_{C-Cl} (Å)	r_{C-O} (Å)	∠COH (°)	$\angle C_1C_2O$ (°)
Regular hexagon				
o-ClC_6H_4OH[a)]	1.713	1.350	120.4	121.9
C_6H_5Cl[b)]	1.712	—	—	—
C_6H_5OH[c)]	—	1.364	109.0	122.2
Distorted hexagon[d)]				
o-ClC_6H_4OH[a)]	1.725	1.350	111.	122.
C_6H_5Cl	1.7248	—	—	—

a) This work. b) Ref. 6. c) Ref. 8. d) Benzene ring structure is that obtained from the r_s-coordinates for chlorobenzene, see Ref. 9.

TABLE 7. QUADRUPOLE SPLITTING OF Q-BRANCH TRANSITIONS (MHz)

Transition	*o*-$^{35}ClC_6H_4OH$		*o*-$^{37}ClC_6H_4OH$	
	Obsd	$\Delta\nu$[a]	Obsd	$\Delta\nu$[a]
$22_{7,15}$—$22_{6,16}$	0.76	0.00		
$23_{7,16}$—$23_{6,17}$	0.57[b]	−0.10		
$17_{8,9}$—$17_{7,10}$	3.15	−0.09		
$18_{8,10}$—$18_{7,11}$	3.14	0.11		
$19_{8,11}$—$19_{7,12}$	2.69	0.05	2.10	−0.06
$20_{8,12}$—$20_{7,13}$	2.07	0.05	1.79	0.00
$21_{8,13}$—$21_{7,14}$	1.28	0.02	1.20	−0.08
$22_{8,14}$—$22_{7,15}$	0.51	0.01		
$23_{8,15}$—$23_{7,16}$	c)		c)	
$24_{8,16}$—$24_{7,17}$	0.46	−0.14	0.31[b]	0.02
$25_{8,17}$—$25_{7,18}$	0.75	−0.01	0.62[b]	−0.09
$15_{8,8}$—$15_{7,9}$	3.29	0.01	2.64	−0.06
$16_{8,9}$—$16_{7,10}$	2.73	−0.11		
$17_{8,10}$—$17_{7,11}$	2.48	0.05	1.74[b]	−0.22
$18_{8,11}$—$18_{7,12}$	2.03	0.00	1.86	0.12
$19_{8,12}$—$19_{7,13}$	1.63	−0.02	1.50	0.05
$20_{8,13}$—$20_{7,14}$	1.35	0.05	1.10	−0.08
$19_{9,10}$—$19_{8,11}$	3.00	0.13		
$20_{9,11}$—$20_{8,12}$	3.06[b]	0.25	2.39[b]	−0.24
$21_{9,12}$—$21_{8,13}$	2.68	0.02	2.15	0.06
$22_{9,13}$—$22_{8,14}$	2.21	−0.10	2.09	0.17
$23_{9,14}$—$23_{8,15}$	1.78	0.04	1.57	−0.01
$24_{9,15}$—$24_{8,16}$	1.07	0.03	1.23	0.11
$25_{9,16}$—$25_{8,17}$	0.5[b]	0.16	0.62	0.00
$26_{9,17}$—$26_{8,18}$	0.3[b]	−0.04	c)	
$27_{9,18}$—$27_{8,19}$	0.67	0.02	c)	
$28_{9,19}$—$28_{8,20}$	0.69	−0.09	0.5[b]	−0.05
$24_{10,14}$—$24_{9,15}$	2.33	−0.05	1.86	−0.01
$25_{10,15}$—$25_{9,16}$	1.99	−0.06	1.68	−0.03
$26_{10,16}$—$26_{9,17}$	1.48	−0.04	1.44	0.02
$27_{10,17}$—$27_{9,18}$	0.95	0.08	0.98	−0.02
$28_{10,18}$—$28_{8,19}$	c)		0.55	0.02
$29_{10,19}$—$29_{9,20}$	0.3[b]	−0.01	c)	
$30_{10,20}$—$30_{9,21}$	0.67	−0.01	c)	
$28_{11,17}$—$28_{10,18}$	1.82	−0.02	1.60	0.03
$29_{11,18}$—$29_{10,19}$	1.44	0.11	1.32	0.02
$30_{11,19}$—$30_{10,20}$	0.71	0.00	1.03	0.13
$31_{11,20}$—$31_{10,21}$	c)		0.5[b]	0.06
$32_{11,21}$—$32_{10,22}$	0.3[b]	−0.10	c)	
$32_{12,20}$—$32_{11,21}$	1.17	0.00	1.26	0.07
$33_{12,21}$—$33_{11,22}$	0.62	0.04	0.79	−0.03
$34_{12,22}$—$34_{11,23}$	c)		0.3[b]	−0.07
$35_{13,22}$—$35_{12,23}$	0.95	−0.09		
$36_{13,23}$—$36_{12,24}$	0.45	−0.02	0.75	0.00

a) $\Delta\nu$=observed−calculated. b) Not included in the least-squares fitting. c) Not resolved.

TABLE 8. QUADRUPOLE COUPLING CONSTANTS OF CHLORINE (MHz)[a]

	$^{35}ClC_6H_4OH$	$^{37}ClC_6H_4OH$
χ_{aa}	-67.6 ± 0.3	-55.9 ± 2.0
χ_{bb}	33.3 ± 0.1	26.5 ± 0.3
χ_{cc}	34.3 ± 0.4	29.4 ± 2.3
θ_{za}[b]	5.69°	4.97°
χ_{zz}[c]	-68.6 ± 1.3[e]	-56.5 ± 4.5[e]
χ_{yy}	34.3 ± 0.9[e]	27.1 ± 1.1[e]
χ_{xx}[d]	34.3 ± 0.4	29.4 ± 2.3

a) a, b, and c are the principal inertial axes. b) θ_{za} is the angle between the principal inertial axis a and the principal z axis. c) χ_{zz} is the component along the C–Cl bond. d) χ_{xx} is the component perpendicular to the molecular plane and χ_{yy} is the in-plane component. e) The uncertainties in the χ-values are estimated from the ambiguity in the angle of θ_{za}, ±1°.

TABLE 9. PRINCIPAL QUADRUPOLE COUPLING CONSTANTS OF ^{35}Cl FOR SEVERAL SUBSTITUTED CHLOROBENZENES (MHz)[a]

	χ_{zz}	χ_{yy}	χ_{xx}	η[b]
o-ClC_6H_4OH[c]	−68.6	34.3	34.3	0.00
C_6H_5Cl[d]	−71.10	—	—	—
o-$C_6H_4Cl_2$[e]	−63.3	32.4	30.9	0.02
m-$C_6H_4Cl_2$[f]	−70.2	37.4	32.8	0.06

a) z-Axis is along the C–Cl bond and y-axis is in the molecular plane. b) $\eta=(\chi_{xx}-\chi_{yy})/\chi_{zz}$. c) This work. d) Ref. 6. e) Ref. 10. f) Ref. 11.

rotational constants in Table 3. The quadrupole coupling constants in the principal inertial axis system, χ_{aa}, χ_{bb}, and χ_{cc}, were obtained using the least-squares method, as shown in Table 8. In this procedure, the inverse of the squared uncertainty, the standard deviation in the measurements of the splitting, was taken as the weight for each line frequency. The uncertainties in Table 8 were calculated from the estimated error in the frequency measurements of the unresolved F components. Assuming that the principal z-axis of the χ-tensor lies on the C–Cl bond, the values of χ_{zz} and χ_{yy} are obtained for the *cis*-form, as given in Table 8. The value of χ_{xx}, the component perpendicular to the molecular plane, is the same as χ_{cc}.

The principal values for several substituted chlorobenzenes are listed in Table 9. The value of χ_{zz} in *o*-chlorophenol is apparently smaller than in monochlorobenzene and *m*-dichlorobenzene. The χ_{zz} values, however, depend on the uncertainty of the transformation angle θ_{za}, ±1° as estimated from the ambiguity in the structure model, so that the differences in the values among these compounds are not very significant. The value around −70 MHz for χ_{zz} is considered to be normal for a chlorine atom which has hydrogen atoms nearby at the ortho position.[11] It seems that the hydrogen-halogen interaction does not have a significant effect on the electronic charge distribution about the chlorine nucleus in this molecule. The same conclusion had been obtained for 2-chloroethanol[5] through its microwave spectrum, where the conformation (*gauche-gauche* form) is favorable for the intramolecular hydrogen bond formation. Although the non-bonded distance between chlorine and hydrogen (2.609 Å for 2-chloroethanol and 2.53 Å for *o*-chlorophenol) is shorter than the sum of the van der Waals radii of chlorine and hydrogen (3.0 Å), no significant effect on the quadrupole coupling constants of chlorine nucleus was observed for *o*-chlorophenol or for 2-chloroethanol.

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