Microwave Spectrum and Molecular Structure of Monochloroacetonitrile, CH_2ClCN

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Since the structure of the monochloroacetonitrile molecule CH_2ClCN is similar to that of propargyl chloride $CH_2ClC\equiv CH$, it is of some interest to compare the structure of the two molecules with each other in detail. In particular, the C—Cl bond length is important in the respect because it will give some information concerning the electronic structure of the molecule. The quadrupole coupling constant of chlorine nucleus is also important for discussing the nature of the C—Cl bond.

When the present investigation was coming nearly to the end, a paper was published by Graybeal on the structure of the CH_2ClCN molecule by the microwave absorption spectrum[1]. But his result seems to involve a number of unreliable data and moreover only two isotopic species, $CH_2{}^{35}ClCN$ and $CH_2{}^{37}ClCN$, were used in his study. The molecular structure and the molecular constants obtained in the present paper would be more reliable than those by Graybeal.

Experimental

The rotational spectra of monochloroacetonitrile, $CH_2{}^{35}ClCN$, $CH_2{}^{37}ClCN$, $CD_2{}^{35}ClCN$, and $CD_2{}^{37}ClCN$, were observed at room temperature by using the recording microwave spectrometer with a 100 Kc. Stark modulation described in the previous paper[2]. The microwave was supplied by klystrons,

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[1] J. D. Graybeal, *J. Chem. Phys.*, **32**, 1258 (1960).

[2] E. Hirota and Y. Morino, This Bulletin, to be published.

TABLE I. OBSERVED AND CALCULATED CENTER FREQUENCIES

	$CH_2{}^{35}ClCN$		$CH_2{}^{37}ClCN$		$CD_2{}^{35}ClCN$		$CD_2{}^{37}ClCN$	
	obs.	calcd.	obs.	calcd.	obs.	calcd.	obs.	calcd.
a-Type								
$2_{1,2}\to3_{1,3}$	17545	17544.20			17190.80	17190.34	16832.86	16833.12
$3_{0,3}\to4_{0,4}$	23966.23	23968.50						
$3_{1,3}\to4_{1,4}$	23385.72	23388.83			22914.78	22914.49		
$4_{1,4}\to5_{1,5}$	29227.24	29230.41	28611.54	28612.16	28633.16	28633.68	28038.14	28039.38
$5_{1,5}\to6_{1,6}$	35065.78	35068.33	34324.38	34326.95	34346.03	34346.84	33636.16	33634.53
b-Type								
$1_{0,1}\to1_{1,0}$	22422.50	22422.48	22332.96	22332.97				
$3_{0,3}\to3_{1,2}$	23192.78	23191.36	23074.41	23074.49	17585.67	17584.56		
$4_{0,4}\to4_{1,3}$	23821.51	23820.40			18304.48	18304.23	18187.47	18185.99
$5_{0,5}\to5_{1,4}$	24625	24623.42			19234.33	19232.49		
$6_{0,6}\to6_{1,5}$	25614.88	25612.08	25409	25405.55	20389.63	20387.74	20192.84	20191.62
$7_{0,7}\to7_{1,6}$	26801	26799.24	26549	26547.20	21791.27	21790.80	21541.20	21540.40
$8_{0,8}\to8_{1,7}$	28201	28199.58	27894	27892.79	23465.04	23463.98	23148.64	23147.47
$9_{0,9}\to9_{1,8}$	29831	29828.87	29458	29457.20	25429.58	25429.40	25034.94	25033.99
$10_{0,10}\to10_{1,9}$	31706	31703.42	31253	31255.89	27708.01	27706.52	27222.44	27219.00
$11_{0,11}\to11_{1,10}$	33842	33839.15	33303	33304.09	30318.90	30308.94		
$12_{0,12}\to12_{1,11}$					33273.50	33239.82	32562.24	32531.71
$13_{0,13}\to13_{1,12}$							35734.94	35655.44
$0_{0,0}\to1_{1,1}$	28120.10	28120.11	27912.08	27912.07				
$1_{0,1}\to2_{1,2}$	33818.58	33817.76	33492.20	33491.20				
$4_{0,4}\to4_{1,3}$	23821.51	23820.40						
$5_{1,5}\to6_{0,6}$	15794.49	15800.49	15038.47	15042.88				
$6_{1,6}\to7_{0,7}$	22551.95	22559.80						
$11_{2,10}\to12_{1,11}$	16468.89	16502.57	14790.03	14823.01				

TABLE II. ROTATIONAL CONSTANTS AND ASYMMETRY PARAMETERS

	$CH_2{}^{35}ClCN$	$CH_2{}^{37}ClCN$	$CD_2{}^{35}ClCN$	$CD_2{}^{37}ClCN$
A	25271.30 Mc./sec.	25122.52 Mc./sec.	19494.88 Mc./sec.	19377.44 Mc./sec.
B	3151.01	3081.13	3119.94	3051.63
C	2848.80	2789.56	2780.81	2724.15
b_p	-6.78471×10^{-3}	-6.57069×10^{-3}	-1.02490×10^{-2}	-9.92993×10^{-3}

Varian X-12 and X-13, and the frequency was multiplied by a silicon crystal. The frequency range covered was 15000 Mc./sec. to 35000 Mc./sec.

The deuterated samples were prepared as follows: a mixture of the normal monochloroacetonitrile, heavy water and a trace of anhydrous sodium carbonate was kept on a hot water bath for a day and then distilled out. The infrared absorption spectrum showed neither the C–H stretching nor the CH_2 deformation bands.

Results

Monochloroacetonitrile is a nearly prolate symmetric top molecule and both a- and b-type transitions were observed. The transitions of the b-type Q-branch, $J_{0,J}\to J_{1,J-1}$, were most easily identified because of their characteristic hyperfine patterns due to the quadrupole moment of the chlorine nucleus ($I=3/2$) and confirmed by plotting the values of $A-(B+C)/2$ and $b_P=(C-B)/(2A-B-C)$. For CH_2ClCN a-type, and b-type R-branch transitions and for CD_2ClCN a-type R-branch transitions were also measured. The observed center frequencies are given in Table I.

The rotational constants of CH_2ClCN were determined by using the transitions, $0_{0,0}\to1_{1,1}$, $1_{0,1}\to1_{1,0}$, and $3_{0,3}\to3_{1,2}$. Unfortunately none of these transitions were measured for CD_2ClCN and the rotational constants were determined by using relatively low-J transitions. The values are listed in Table II. The center frequencies calculated by using these constants are compared with the observed ones in Table I. (a rigid rotor calculation).

For $CH_2{}^{35}ClCN$ rough estimation of centrifugal effect is made (Table III) by assuming the expression for a symmetric top molecule, $-D_JJ^2(J+1)^2-D_{JK}J(J+1)K_{-1}{}^2-D_KK_{-1}{}^4$. The transitions used for determining the centrifugal constants are $4_{0,4}\to4_{1,3}$, $5_{1,5}\to6_{1,6}$, $5_{1,5}\to6_{0,6}$, $6_{1,6}\to7_{0,7}$, and $11_{2,10}\to12_{1,11}$. The center frequencies calculated with the centrifugal distortion correction are compared with the observed

TABLE III. EFFECT OF THE CENTRIFUGAL DISTORTION FOR $CH_2{}^{35}ClCN$

($D_J=0.004399$ Mc./sec., $D_{JK}=-0.02340$ Mc./sec., $D_K=0.3398$ Mc./sec.)

	ν_{rigid}	$D_{\text{corr.}}$	$\nu_{\text{corr.}}$	$\nu_{\text{obs.}}$
$2_{1,2}\rightarrow 3_{1,3}$	17544.20	−0.33	17543.87	17545
$3_{0,3}\rightarrow 4_{0,4}$	23968.50	−1.13	23967.37	23966.23
$3_{1,3}\rightarrow 4_{1,4}$	23388.83	−0.94	23387.89	23385.72
$4_{1,4}\rightarrow 5_{1,5}$	29230.41	−1.97	29228.44	29227.24
$5_{1,5}\rightarrow 6_{1,6}$	35068.33	−3.52	35064.81	35065.78
$1_{0,1}\rightarrow 1_{1,0}$	22422.48	−0.29	22422.19	22422.50
$3_{0,3}\rightarrow 3_{1,2}$	23191.36	−0.06	23191.30	23192.78
$4_{0,4}\rightarrow 4_{1,3}$	23820.40	0.13	23820.53	23821.51
$5_{0,5}\rightarrow 5_{1,4}$	24623.42	0.36	24623.78	24625
$6_{0,6}\rightarrow 6_{1,5}$	25612.08	0.64	25612.72	25614.88
$7_{0,7}\rightarrow 7_{1,6}$	26799.24	0.97	26800.21	26801
$8_{0,8}\rightarrow 8_{1,7}$	28199.58	1.35	28200.93	28201
$9_{0,9}\rightarrow 9_{1,8}$	29828.87	1.77	29830.64	29831
$10_{0,10}\rightarrow 10_{1,9}$	31703.42	2.23	31705.65	31706
$11_{0,11}\rightarrow 11_{1,10}$	33839.15	2.75	33841.90	33842
$0_{0,0}\rightarrow 1_{1,1}$	28120.11	−0.31	28119.80	28120.10
$1_{0,1}\rightarrow 2_{1,2}$	33817.76	−0.34	33817.42	33818.58
$4_{0,4}\rightarrow 4_{1,3}$	23820.40	0.12	23820.52	23821.51
$5_{1,5}\rightarrow 6_{0,6}$	15800.49	−4.16	15796.33	15794.49
$6_{1,6}\rightarrow 7_{0,7}$	22559.80	−6.63	22553.17	22551.95
$11_{2,11}\rightarrow 12_{1,11}$	16502.57	−34.01	16468.56	16468.89

TABLE IV. MOLECULAR CONSTANTS OF MONOCHLOROACETONITRILE

(Graybeal's values are also given for comparison.)

Present
 Calculated
  C—Cl 1.7815 Å, C—H 1.0881 Å, H···H 1.7812 Å, ∠CCCl 111°29′,
  ∠CCH 107°27′, $\Delta=0.2194$ amu Å², $\chi_{aa}=-32.8$ Mc./sec., $\chi_{bb}=-7.2$ Mc./sec.
 Assumed
  C—C 1.458 Å, C—N 1.158 Å, ∠CCN 180°,

Graybeal
 Calculated
  C—Cl 1.767 Å, C—C 1.472 Å, H···H 1.728 Å, ∠CCCl 111°24′,
  $\chi_{aa}=-30.45$ Mc./sec., $\chi_{bb}=-7.73$ Mc./sec.,
 Assumed
  C—H 1.070 Å, C—N 1.158 Å, ∠CCN 180°, ∠CCH 109°30′.

ones in Table III. It is seen that the discrepancy found in the rigid rotor calculation is largely reduced, even for high-J transitions.

Since only two hydrogen atoms are located above and below the symmetry plane, the distance between them r is given by[2]

$$r=[(I_a+I_b-I_c+\Delta)/m]^{1/2}$$

where Δ is a quantity similar to the inertia defect and m is the mass of hydrogen or deuterium atom. The values of Δ and r (Table IV) were determined by means of the method of least-squares using the four equations given by the four isotopic species.

The number of the rotational constants obtained is twelve. Four of them are used in obtaining the hydrogen to hydrogen distance, hence there remain eight constants for determining the other structural parameters, d_{C-C}, d_{C-Cl}, d_{C-H}, $d_{C\equiv N}$, ∠CCCl, ∠CCH, and ∠CCN. Since isotopes of carbon and nitrogen atoms were not available, none of these parameters could be determined. The C–C bond length adjacent to the triple bond is usually about 1.458 Å, and the C≡N bond length in cyano group is reported for a number of molecules to be 1.158 Å[3]. The assumption of the linear structure for the C—C≡N group may not influence the other structural parameters. Thus the following values were assumed: $d_{C-C}=1.458$ Å,

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3) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, 30, 777 (1959).

TABLE V. COMPARISON OF THE CENTER FREQUENCIES ($CH_2{}^{35}ClCN$) GIVEN BY GRAYBEAL AND BY THE PRESENT AUTHORS

	obs.		calcd.	
	Graybeal	Present	Graybeal*	Present**
a-Type				
$2_{1,2}\to3_{1,3}$	17550	17545	17549.40	17550.06
$3_{0,3}\to4_{0,4}$	23974	23966.23	23975.39	23975.42
$3_{2,2}\to4_{2,3}$	24002		24003.65	24003.66
$3_{3,1}\to4_{3,2}$	24011		24012.09	24012.11
$3_{3,0}\to4_{3,1}$	24011		24012.21	24012.23
$3_{2,1}\to4_{2,2}$	24036		24034.28	24034.28
b-Type				
$5_{1,5}\to6_{0,6}$	15794.54	15794.49	15794.54	15795.07
$10_{1,10}\to9_{2,7}$	16347.33		16347.34	16337.31
$11_{2,10}\to12_{1,11}$	16469.00	16468.89	16469.00	16467.53
$6_{1,6}\to7_{0,7}$	22554.00	22551.95	22553.57	22555.14
$4_{0,4}\to4_{1,3}$	23829.80	23821.51	23830.09	23830.39

* Values cited from Graybeal's paper. No corrections for centrifugal effects.

** Values calculated by using the rotational constants given by Graybeal. No corrections for centrifugal effects.

$d_{C\equiv N}=1.158$ Å, and $\angle CCN=180°$. The remaining five parameters were determined by the method of least-squares using the values of A and B, as shown in Table IV.

Nuclear quadrupole coupling constant is calculated for $CH_2{}^{35}ClCN$ from the transitions $1_{0,1}\to1_{1,0}$, $3_{0,3}\to3_{1,2}$, and $6_{0,6}\to6_{1,5}$, and given in Table IV. If the electronic charge distribution about the C—Cl bond is assumed to be cylindrical, the quadrupole coupling constant along the C—Cl bond axis is -80 Mc./sec. The value is consistent with that observed in the solid state, 76.25 Mc./sec.[4] The hyperfine structures due to the nitrogen nucleus were not resolved.

Discussion

A quite normal value 1.7815 Å is obtained for the C—Cl bond length, which is very close to the value obtained for propargyl chloride, 1.780 Å[2], hence it is sure that neither a double bond structure nor an ionic structure contributes so much to the electronic configuration in the ground state of this molecule.

The center frequencies measured by Graybeal[1] are shown in Table V. Some of them are confirmed by the present investigation within the experimental error, but others show a definite discrepancy. Graybeal calculated the center frequencies by using the rotational constants given in Table VI. However, some of them are also in error by as much as 10 Mc./sec. It is found that the δ expansion formula he used[5] is insufficient for calculating the energy of the rotational states with J as high as ten. As a result his values of A are larger than the present ones by about 13 Mc./sec. (Table VI). On the other hand the constants of the present paper reproduce the frequencies of low-J transitions in good agreement with the observed ones. If the centrifugal distortion is taken into account, the rotational constants given in the present paper would account even for high-J transitions (Table III).

TABLE VI. COMPARISON OF THE ROTATIONAL CONSTANTS (IN Mc./sec) OBTAINED BY GRAYBEAL AND BY THE PRESENT AUTHORS

	$CH_2{}^{35}ClCN$		$CH_2{}^{37}ClCN$	
	Graybeal	Present	Graybeal	Present
A	25284.77	25271.30	25135.17	25122.52
B	3151.61	3151.01	3081.77	3081.13
C	2849.90	2848.80	2790.84	2789.56

Graybeal reported the C—Cl bond length to be 1.767 Å and the C—C bond length to be 1.472 Å (Table IV). If isotopic species of carbon or nitrogen atoms were not available as in his study, it would be difficult to determine these two parameters separately. The correction due to the inertia defect has not been taken in the H⋯H distance obtained by Graybeal, thus the structure of the CH_2 group reported by him is not reliable.

The value of the quadrupole coupling constant of chlorine nucleus is observed to be -80 Mc./sec., which is slightly higher than that of propargyl chloride (-75.8 Mc./sec.)[2]

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[4] J. D. Graybeal and C. D. Cornwell, *J. Phys. Chem.*, **62**, 483 (1958).

[5] Graybeal used likely the expansion formula given by King, Hainer and Cross [*J. Chem. Phys.*, **11**, 27 (1943)].

or of ethyl chloride (−70.07 Mc./sec.)[6]. This fact may be accounted for by the presence of the electronegative cyano group, since this reduces the ionic structure of the C—Cl bond. The present value of the quadrupole coupling constant of chlorine nucleus would be more reasonable than Graybeal's value −76.36 Mc./sec., since the (absolute) value obtained in the vapor phase is usually larger than that in the solid phase by several megacycles and the coupling constant of monochloroacetonitrile is 76.25 Mc./sec. in the solid state.

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[6] R. S. Wagner and B. P. Dailey, ibid., 26, 1588 (1957).