

Notes

Microwave Spectrum, Structure, Dipole Moment, and Quadrupole Coupling Constant of Propargyl Chloride

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PAULING, Gordy, and Saylor¹ found by the electron diffraction that the C—Cl bond length in propargyl chloride $\text{CH}_2\text{ClC}\equiv\text{CH}$ was 1.82 ± 0.02 Å, remarkably longer than the usual value of 1.77 Å. They explained the anomalous bond length by considering a resonance structure, $\text{Cl}^-\text{CH}_2=\text{C}=\text{C}^+\text{H}$. If this structure has a significant contribution, a large dipole moment and a small quadrupole coupling constant of chlorine nucleus should be expected. However, recent measurement of dielectric constant² gave the dipole moment of only $1.65D$, rather small in magnitude compared with $2.05D$ of ethyl chloride. Anomaly was not found in the measurement of the quadrupole coupling constant of chlorine nucleus in the solid state, the result being 71.6246 Mc/sec at 77°K.³ In this respect an investigation by the microwave spectroscopy is desirable, since it gives not only the precise structure but also the dipole moment and the quadrupole coupling constant simultaneously.

The apparatus used was a spectrometer equipped with a 100-kc crystal oscillator for the Stark modulation. The observed spectra assigned definitely are listed in Table I. In addition to these lines, many high- J transitions (probably the b -type R -branch) and transitions from the molecules of the vibrationally excited states were observed. From the observed data the rotational constants and the asymmetry parameters were determined as shown in Table II. The effect of the centrifugal distortion was clearly observed, but the exact treatment was difficult to be carried out.

The H···H distance in CH_2Cl group is given by the quantity $I_a + I_b - I_c$, hence the structure of the framework is determined by four rotational constants, that

TABLE I. Observed and calculated spectra (in Mc/sec).^a

	CH ₂ Cl ³⁵ C≡CH		CH ₂ Cl ³⁷ C≡CH	
	ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}
a-type				
2 ₀₂ -3 ₀₃	17 559.49	17 559.47		
2 ₁₂ -3 ₁₃	17 117.56	17 117.51		
2 ₁₁ -3 ₁₂	18 023.67	18 023.22		
3 ₀₈ -4 ₀₄	23 397.50	23 397.48		
3 ₁₈ -4 ₁₄	22 819.50	22 819.59		
3 ₁₂ -4 ₁₃	24 027.56	24 028.26	23 520.66	23 520.91
3 ₂₂ -4 ₂₃	23 428.80	23 429.2		
3 ₂₁ -4 ₂₂	23 460.76	23 460.52		
3 ₂₁ -4 ₂₂	29 222.55	29 222.29	28 618.03	28 617.83
4 ₀₄ -5 ₀₅	28 518.16	28 518.24	27 936.02	27 936.00
4 ₁₄ -5 ₁₅	29 281.64	29 281.78	28 673.52	28 672.8
4 ₂₂ -5 ₂₄	29 345.55	29 345.7		
4 ₂₂ -5 ₂₃				
4 ₃₁ -5 ₃₂	29 302.58	29 302.15	28 693.31	28 694.4
4 ₃₂ -5 ₃₃				
4 ₁₃ -5 ₁₄			29 394.71	29 394.
b-type				
4 ₀₄ -5 ₁₄	22 921.45	22 921.58		
4 ₀₄ -5 ₁₄	23 726.93	23 727.87		
5 ₀₅ -6 ₁₅	24 719.60	24 719.31	24 509.33	24 508.91
6 ₀₆ -6 ₁₅	25 913.52	25 911.16	25 659.00	25 656.94
7 ₀₇ -7 ₁₆	27 324.86	27 319.22	27 016.84	27 011.07
8 ₀₈ -8 ₁₇	28 972.01	28 958.40	28 600.14	28 587.43
9 ₀₉ -9 ₁₈	27 077.01	27 077.01	26 868.46	26 868.46
0 ₀₀ -1 ₁₁	29 130.80	29 132.01		
7 ₁₇ -8 ₀₈	17 433.14	17 442.95		
11 _{2,10} -12 _{1,11}	25 071.70	25 079.7		
12 _{2,11} -13 _{1,12}				

^a The centrifugal distortion was assumed to be

$$-D_{JK}J(J+1)K-1^2-D_JJ^2(J+1)^2,$$

with $D_{JK} = -0.057$ Mc/sec and $D_J = 0.0021$ Mc/sec.

is, two from each isotopic molecule. Since parameters concerning hydrogen atoms have minor contributions to the rotational constants and the length of the C≡C bond is usually found to be 1.207 Å⁴ irrespective of the attached groups, reasonable assumptions have been made on these parameters as listed in Table III. Then the length of the C—Cl bond was 1.7802 Å, the error being smaller than 0.005 Å. One can see that the result is not strongly influenced by the assumptions, because the mass of chlorine atom is much larger than those of carbon and of hydrogen atoms. Thus it was concluded that the C—Cl bond length reported by Pauling, *et al.*, was in considerable error and the discrepancy between the bond length and the electronic measurements mentioned above was completely solved.

The quadrupole coupling constant was calculated from well-resolved eight lines. The two components along the *a*- and *b*-axes, χ_{aa} and χ_{bb} , were found to be

TABLE II. Rotational constants and asymmetry parameters of propargyl chloride.

	CH ₂ Cl ³⁵ C≡CH	CH ₂ Cl ³⁷ C≡CH
A	24 299.28±0.50 Mc/sec	24 146.48±0.50 Mc/sec
B	3 079.77±0.20 Mc/sec	3 013.80±0.20 Mc/sec
C	2 777.73±0.20 Mc/sec	2 721.98±0.20 Mc/sec
δ	0.014035±0.000018	0.013621±0.000018

TABLE III. Molecular constants of propargyl chloride.

C—Cl	1.7802 Å	H...H(CH ₂ Cl)	1.708 Å
C—C	1.458 Å	∠CCCl	112°9'
assumptions: C≡C	1.207 Å	C—H (C≡CH)	1.06 Å
C—H (CH ₂ Cl)	1.09 Å	∠CCH	111°30'
χ_{aa}	= -30.4 Mc/sec	μ_{total}	= 1.68±0.04 D
χ_{bb}	= -7.5 Mc/sec	($\mu_a = 0.99 D, \mu_b = 1.36 D$)	

−30.4 Mc/sec and −7.5 Mc/sec, respectively. If the electrostatic potential along the principal axis is cylindrically symmetric, the coupling constant along the principal axis is −75.8 Mc/sec, consistent with the value measured in the solid state, 71.6246 Mc/sec.

The dipole moment was determined from the Stark effect of the 0₀₀→1₁₁ line. The Stark effect of this line was complicated by the quadrupole coupling of chlorine nucleus, but the detailed study allowed for the simultaneous determination of two components, μ_a and μ_b , which were found to be 0.99D and 1.36D, respectively. Thus the total dipole moment was 1.68±0.04D, in good agreement with the value of 1.65D obtained from the dielectric constant measurement. It seems most plausible that the negative direction of the dipole moment lies between the C—Cl and the C—C≡C—H bonds, at an angle of 16°±7° from the former.

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¹ Pauling, Gordy, and Saylor, *J. Am. Chem. Soc.* **64**, 1753 (1942).² Chiba, Shimozawa, Miyagawa, and Morino, *Bull. Chem. Soc. Japan* **30**, 223 (1957).³ Shimozawa, Chiba, Miyagawa, and Morino (to be published).⁴ Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), Table A. 9.; Thomas, Sherrard, and Sheridan, *Trans. Faraday Soc.* **51**, 619 (1955); C. C. Costain, *J. Chem. Phys.* **23**, 2037 (1955).