Pure Quadrupole Spectra of Propargyl Chloride and its Related Compounds

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In the preceding papers[1], the molecular structures of propargyl chloride and its related compounds were discussed on the basis of the observed dipole moments. The results obtained so far are listed in Table I. It can readily be seen that the C–Cl bond moment in these compounds is smaller than the average value of the usual C–Cl bond moment of the halogenated saturated hydrocarbons (1.86 D), except in the case of monochlorobutyne-2. The early investigation gave a considerably longer C–Cl distance for the bond which is adjacent to a triple bond[2]. Pauling explained

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1) Y. Morino, I. Miyagawa, T. Chiba and T. Shimozawa, This Bulletin, **30**, 222 (1957); T. Chiba, T. Shimozawa, I. Miyagawa and Y. Morino, ibid., **30**, 223 (1957).

2) L. Pauling, W. Gordy and J. H. Saylor, *J. Am. Chem. Soc.*, **64**, 1753 (1942).

TABLE I. THE STRUCTURAL PARAMETERS OF PROPARGYL HALIDES AND ITS RELATED COMPOUNDS

$HC{\equiv}C\text{-}CH_2Cl$	Pauling[2] (Electron diffraction)	r(C-Cl)	1.82 A
Propargyl chloride	Morino[1] (Dipole moment)	μ(C-Cl)	1.76 D
$HC{\equiv}C\text{-}CH_2Br$	Rogers[3] (Dipole Moment)	μ(C-Br)	1.62 D
Propargyl bromide			
$ClH_2C\text{-}C{\equiv}C\text{-}CH_2Cl$	Morino[1] (Dipole moment)	μ(C-Cl)	1.57 D
1,4-Dichloro-2-butyne	Kuchitsu[7] (Electron diffraction)	r(C-Cl)	1.79 A
$H_3C\text{-}C{\equiv}C\text{-}CH_2Cl$	Morino[1] (Dipole moment)	μ(app.)	2.17 D
1-Chlorobutyne-2			

TABLE II. NUCLEAR QUADRUPOLE COUPLING CONSTANTS AND APPARENT DIPOLE MOMENT OF PROPARGYL CHLORIDE AND ITS RELATED COMPOUNDS

	at 77°K	(eq$Q$)	μ(app.)
Propargyl chloride	35.812,3 Mc.	71.6 Mc.	1.65 D
1-Chlorobutyne-2	35.361,8 Mc.	70.7 Mc.	2.17 D
1,4-Dichloro-2-butyne	36.372,8 Mc.	72.6 Mc.	1.47 D

this lengthening of the C-Cl bond in propargyl chloride by assuming that the resonance form II makes a large contribution to the structure. However, the experimental results on the bond moment stated above contradict this explanation. Rogers[3] attributed this small dipole moment to the presence of structure III.

$$\underset{\text{I}}{HC{\equiv}C\text{-}CH_2Cl}, \quad \underset{\text{II}}{HC^+{=}C{=}CH_2Cl^-}$$

$$\underset{\text{III}}{HC^-{=}C{=}CH_2Cl^+}$$

As is well known, the electric quadrupole coupling constant (eq$Q$) obtained from the pure quadrupole spectra provides us with information on the charge distribution of the chemical bond[4]. If the distribution of the electron is spherically symmetric, as it is in a free Cl-ion, the eq$Q$ constant vanishes, whereas it must be quite large in the case of Cl^+, where two unbalanced p-electrons exist. Therefore, it seemed of interest to measure the pure quadrupole resonance spectra of propargyl chloride and its related compounds to obtain some information about the electronic structure of the C–Cl bond in these compounds. The experimental method used is the same as that reported previously[5]. The results are listed in Table II.

A linear relation was previously pointed out[5] between the nuclear quadrupole coupling constants and the apparent C–Cl bond moment of the halogen derivatives of saturated hydrocarbons, as is shown in Fig. 1. Using the bond moments, 1.65 D, 2.17 D and 1.47 D, derived from the observed dipole moments[1],

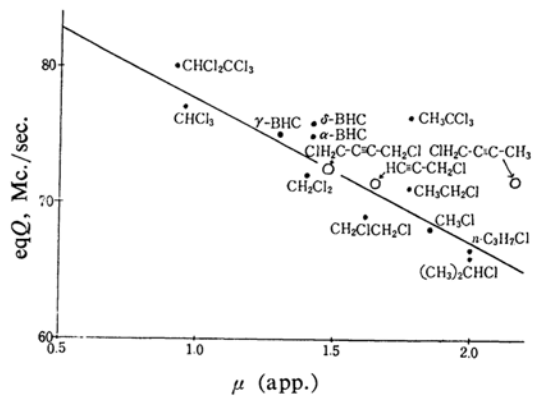

Fig. 1. Relation between eq$Q$ and apparent C–Cl bond moment.

the eq$Q$ constants of the three compounds are plotted on this diagram with white circles. They are in good agreement with the straight-line relation for the saturated hydrocarbons, though in the case of monochlorobutyne-2 a sight discrepancy from the line is apparent. It may be concluded, therefore, that the electronic states of the C–Cl bond in these molecules are nearly the same as those of the halogenated saturated hydrocarbons: the presence of a triple bond in the molecule has no great effect on the local C–Cl bond structure. It should be noted here that recent microwave study of propargyl chloride has confirmed the normal value, 1.78 A, of the C–Cl bond distance of this molecule[6].

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6) E. Hirota, T. Oka and Y. Morino, ibid., **29**, 444 (1958).
7) K. Kuchitsu, This Bulletin, **30**, 391 (1956).