Dipole Moment and Bond Character of Propargyl Halides and Mono- and Di-chlorobutynes

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In the preceding paper[1] it was shown that the C—Cl bond moment of 1, 4-dichlorobutyne was abnormally small. This is an unexpected result from the current resonance theory. In order to elucidate this circumstance, a measurement was made on the dipole moments of propargyl chloride and bromide, and monochlorobutyne in the gaseous state. Quite recently Rogers and Panish[2] made a study on the dipole moments of similar compounds including propargyl bromide and iodide. Although their measurement was made in solution, the results agreed substantially with the present one.

Experimental

Propargyl chloride was prepared by the chlorination[3] of propargyl alcohol with phosphorus trichloride in the presence of pyridine at about 0°C. The raw product was washed with ice-

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[1] Y. Morino et al., This Bulletin, **30**, 222 (1957).

[2] M. T. Rogers and M. B. Panish, *J. Am. Chem. Soc.*, **77**, 3684 (1955).

[3] L. F. Hatch and V. Chiola, ibid., **73**, 360 (1951).

water and fractionated: b. p. 56-57°C.

Propargyl bromide was fractionated from a commercial product of General Anilin and Film Corps.: b. p. 83-84°C.

1-Chloro-2-butyne was prepared from an isomeride of 1,3-dichloro-2-butene (b. p. 66-67°C/95 mmHg) by the following procedure[4]: first dichlorobutene was hydrated to 1-chloro-2-butene-3-ol (b. p. 93-94°C/50 mmHg) by boiling with sodium carbonate solution. This alcohol was dehydrochlorinated to 2-butene-1-ol (b. p. 90-96°C/95 mmHg) by boiling with a concentrated solution of potassium hydroxide. 2-Butyne-1-ol was chlorinated to 1-chloro-2-butyne by the method used for propargyl chloride. The fractionated product had the boiling point of 104-107°C.

The apparatus and the procedure of the measurement of the dipole moments is described elsewhere[5].

Results and Discussions

The results of the measurement of the dipole moments are given in Table I.

As regards propargyl chloride, Pauling et al.[6] proposed the following resonance structure for the explanation of the longer C—Cl distance;

(A) $HC\equiv C-CH_2Cl$

and (B) $H-C^+=C=CH_2\ Cl^-$.

If it is true, the dipole moment of propargyl chloride will be large, because the form (B) has a large moment (ca. 18 *D*) due to the positive charge at the carbon atom and the negative charge at the chlorine atom. The observed values 1.65 *D* of chloride and 1.52 *D* of bromide do not show any trace of this tendency. Therefore, it is impossible to take this resonance formula for the main structure of propargyl chloride.

This anomalous feature is more distinct when propargyl halides are compared with the corresponding compounds having a double bond. The moment of allyl chloride, 1.98 *D*[7], is somewhat less than that of propyl chloride, 2.10 *D*[8]. As Smyth has pointed out[7], the difference between them can be explained by taking into account a hyperconjugation of

(C) $C^1H_2=C^2H-C^3H_2Cl$

and (D) $H_2C^- -CH=CHCl\ H^+$.

According to this opinion, the observed moment 0.35 *D* of propylene molecule itself may be ascribed to this hyperconjugation, and, if this hyperconjugation is not disturbed by the substitution of a chlorine atom, the moment of allyl chloride will be calculated by taking a resultant of the two dipoles, one in the C–Cl bond direction,

TABLE I

RESULTS OF THE MEASUREMENT OF THE DIPOLE MOMENT IN THE GASEOUS STATE

Temp. K	No. of obs.	Press. range mmHg	Molar polarizn. cc.	Mean deviatn. of polarizn. cc.	Dipole moment *D*
Propargyl chloride					
$MR_D=18.8$ cc.a) $P_E+P_A=19.7$ cc.					
294.3	7	26-56	76.2	0.1	1.65_2
326.3	9	54-79	70.8	0.4	1.65_3
					av. 1.65_3
Propargyl bromide					
$MR_D=22.1$ ccb) $P_E\div{}_A=23.2$ cc.					
306.3	8	45-77	69.2	0.3	1.52_1
349.8	9	54-93	63.6	0.7	1.52_3
373.3	8	67-95	60.6	0.3	1.51_4
					av. 1.51_9
1-Chloro-2-butyne					
$MR_D=23.7$ cc.a) $P_E+P_A=24.9$ cc.					
328.4	8	51-59	113.1	0.6	2.18_0
354.4	10	57-85	105.5	1.0	2.16_5
385.6	9	61-91	99.6	0.8	2.17_4
					av. 2.17_3

a) Ref. (3)

b) Ref. (2)

$P_E+P_A=1.05\ MR_D$ is assumed throughout.

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[4] M. S. Schechter et al., idid., **74**, 4903 (1952).

[5] T. Chiba, This Bulletin, **28**, 19 (1955), refer also to the forthcoming paper on the dipole moment of cyclohexadione.

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

[7] N. B. Hanney and C. P. Smyth, ibid., **68**, 1005 (1946).

[8] Groves and Sugden, *J. Chem. Soc.*, **1937**, 158.

and the other, that of the propylene skeleton, in the direction of the $C^2—C^3$ bond*. Thus, by substrating $0.35\,D$ vectorially from the observed moment of allyl chloride, $1.98\,D$, the apparent C—Cl moment is calculated to be $2.08\,D$, which can be compared with the moment of the propyl chloride, 2.10 D. It will be permissible to consider that this is the moment which the form (C) has when the effect of the form (D) is eliminated.

Now, in case of propargyl halides, in order to obtain the apparent C—Cl moment eliminating the contribution from the C≡C—C skeleton, the same kind of correction should be made by taking the moment of methyl acetylene, $0.75\,D$, as the moment of the C≡C—C skeleton on the molecular axis. The observed moments of propargyl chloride, $1.65\,D$, and bromide, $1.52\,D$, yield $1.76\,D$ and $1.62\,D$, which are less than those of the corresponding saturated chloride and bromide by $0.28\,D$ and $0.40\,D$ respectively. According to Rogers[2], this tendency is much more prominent in the case of propargyl iodide, the difference being $-0.60\,D$**. Thus we have no evidence for the increase of the moments of propargyl halides, so that it is difficult to regard Pauling's resonance structure as a significant contribution to these compounds.

As described in the preceding paper, the component of the CH_2Cl-group moment perpendicular to the C—C axis in dichlorobutyne was found to be $1.47\,D$, assuming free internal rotation, which is definitely smaller than the value $1.74\,D$ calculated on the basis of the usual C-Cl bond moment, $1.86\,D$, and of the C—C—Cl angle of 111°[9]. This cannot be accounted for by the mutual induction of the two C—Cl bonds as found in case of 1,2-dichloroethane, since the C—Cl dipoles are far apart in this compound (ca. 5A). Now, if the resonance scheme proposed by Pauling takes place in this molecule too, the following structures are to be taken into account, both of which would bring about the increase of the perpendicular component of the C—C bond moment:

$$\text{(E)}\quad Cl—CH_2—C^+=C=CH_2Cl^-$$

and $$\text{(F)}\quad Cl^-H_2C=C=C^+—CH_2Cl.$$

Hence there is another evidence against Pauling's resonance structure.

For monochlorobutyne the measurement of the dipole moment is promising because this molecule has a symmetrical structure of carbon skeleton with no dipole moment, so that it will provide a direct estimation of the C—Cl bond moment in these molecules. The observed moment, $2.17\,D$, is unexpectedly large and really almost equal to that of the corresponding saturated compound***. Rogers attributed the small dipole moments and the long C—X bond distances of propargyl halides to the contribution of the following resonance formulas:

$$\text{(G)}\quad H—C\equiv C—CH_2^-\ X^+$$

and $$\text{(H)}\quad H—C^-=C=CH_2\ X^+$$

The dipole moments of propargyl halides are explained by this resonance, but the C—I bond should have larger increase than does the C—Cl bond, because the moment decrease was found to be pronounced in propargyl iodide compared with the chloride. The C—Br and C—I distances observed by Pauling et al.[6] seem to be practically normal. In addition,the large moment of monochlorobutyne described above cannot be explained by this resonance scheme alone.

If the valence angles and bond moments are assumed to be the same in the three compounds: propargyl chloride, mono- and di-chlorobutynes, the most plausible way to make all moments of these compounds consistent is to take the group moments and their directions as follows:

1. The C—Cl bond moment is $1.58\,D$ along the bond direction.
2. The methyl acetylene skeleton of propargyl chloride has a moment $0.75\,D$ along the axis of C≡C—C.
3. A moment of $0.93\,D$ is induced in the direction of the C≡C—C bond in propargyl chloride, and a moment of $1.04\,D$ is induced in monochlorobutyne.

The moment of C—Cl bond, $1.58\,D$, is obtained by use of the perpendicular component of dichlorobutyne, $1.47\,D$, and of the C—C—Cl angle of 111° (see Fig. 1(a)). If this value is kept in the molecule of monochlorobutyne and of propargyl chloride, the vector addition will not hold unless an induced moment is taken into

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* Strictly speaking, the moment induced by the hyperconjugation is not in the direction of C^2-C^3 bond, but, considering the possible positions of the C^1-H_2-group, the above assumption on the direction of this moment may be justified.

** Rogers took $0.80\,D$ for methyl acetylene moment.

9) Y. Morino and K. Kuchitsu, This Bulletin, (to be published).

*** If the sample we prepared were 3-chloro-1-butyne, it could be expected to give a dipole moment as high as $2\,D$. However, the boiling point and the refractive index of our sample agreed with those in the literature, and the configuration 1-chloro-2-butyne was already verified in organic chemical process (Ref. 3. p. 362).

consideration. If we assume that this induced moment is along the direction of the molecular axis, the value of $1.04\,D$ will be obtained for monochlorobutyne (see Fig. 1(b)). Similar consideration gives the value of $0.93\,D$ for the induced moment in propargyl chloride in the direction of the molecular axis, using $0.75\,D$ as the moment of the skeleton of $C\equiv C-C$ (see Fig. 1(c)). Thus it must be concluded that the moment of the $C-Cl$ bond attached to the α position of a $C\equiv C$ bond is $0.3\,D$ smaller than the usual value and is accompanied with a fairly large moment lying on the axial direction.

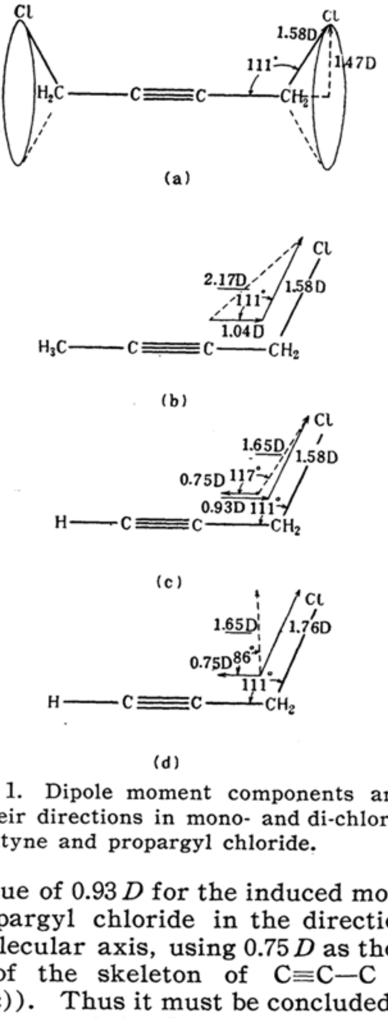

Fig. 1. Dipole moment components and their directions in mono- and di-chlorobutyne and propargyl chloride.

Of course this is a tentative conclusion, ignoring a possible difference of the bond moments from one compound to another, as well as the difference in the direction of the induced moments. At first sight, this result may look untrustworthy and peculiar, but a similar phenomenon was found recently by microwave spectroscopy in case of propiolic aldehyde $H-C\equiv C-CHO$⁽¹⁰⁾. It was concluded that the total moment of $2.46\,D$ does not lie along the direction of the $C=O$ bond, but in the direction close to the $C\equiv C-C$ axis, making an angle of 25-30°with the carbonyl bond direction. This situation is just similar to the case of the chlorine compounds described above.

If the above argument is the case, the resultant moment of propargyl chloride lies along the direction making an angle of 117° with the molecular axis (Fig. 1(c)). On the contrary, if the moment of this compound is composed only of a moment of the $C-Cl$ bond and of methyl acetylene skeleton, as shown in the Fig. 1(d), the resultant should lie in the direction of 86° with the axis. Therefore, it is desirable to determine the direction of the total moment of propargyl chloride by means of microwave spectroscopy, which will make a choice between the alternatives stated above.

Recently Mr. I'Haya calculated the dipole moment of propargyl chloride by the method of MO theory⁽¹¹⁾. His result is in excellent agreement with the observed value reported here. The same calculation, however, cannot be applied to dichlorobutyne, because it does not give the dipole moment found by the measurement.

I'Haya suggested us that the induction moment along the $C\equiv C-C$ axis given in Fig. 1(b) and (c) can reasonably be made smaller from the following reason. The hyperconjugation which takes place in methyl acetylene is twice as large as that in propargyl halide, since the $-CH_3$ group forms two mutually perpendicular "π-type orbitals", each of which is equivalent to that formed by $-CH_2$ group. Therefore, if the moment of methyl acetylene is entirely due to hyperconjugation, $0.38\,D$ must be assumed for the moment of the $C\equiv C-C$ skeleton in propargyl chloride instead of $0.75\,D$. This enables one to reduce the inductive moment in propargyl chloride to a more reasonable value $0.56\,D$. Similarly, in monochlorobutyne one can expect that skeletal moment does not vanish but has a value $0.38\,D$. This reduces an induction moment to $0.67\,D$ in this compound.

Summary

The dipole moments of propargyl chloride, bromide and monochlorobutyne in the gaseous state are measured to be $1.65\,D$,

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10) J. A. Howe and J. H. Goldstein, *J. Chem. Phys.*, **23**, 1223 (1955).

11) I'Haya, presented at the Discussion Meeting of Structural Chemistry held in Tokyo by the Chemical Society of Japan on October, 1955.

1.52 *D* and 2.17 *D* respectively. The moment of propargyl chloride and bromide are considerably smaller than the saturated one even though the correction of C≡C—C skeletal moment is taken into account. This is consistent with the $-CH_2Cl$ group moment of dichlorobutyne obtained in the preceding work. These results are inconsistent with the resonance scheme presented by Pauling et al. for propargyl halide. The anomaly is considered as a characteristic feature of the molecules having triple bonds of this kind. By taking all of the moments of dichloro- and monochlorobutynes and propargyl chloride into account, the bond moments, the induction moments and the direction of the resultants are predicted as shown in Fig. 1.

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