# *The Dipole Moments of Some Polyhalocyclohexanes and their Related Compounds. I.*

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As is well known, it is possible for the atoms attached to a carbon atom of the cyclohexane ring to exist at two positions: the polar and the equatorial ones, with regard to the relative direction of the bonds to the plane of the ring.[1,2,3a] It follows that a polysubstituted compound of cyclohexane has a lot of geometrical isomers. A good example is the case of BHC: it has actually six isomers, $\alpha$ to $\eta$ forms,[4] due to the various combinations of the polar and equatorial bonds, and its $\gamma$-isomer is characterized by its mar-

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[1] O. Hassel and E. Naeshagen, *Tids. Kjemi Bergvesen Met.* **10**, 126 (1930).

[2] K. Kojima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).

[3] R. Riemschneider. a) Communication XXI. . . . The method of representation of the chair form of cyclohexane ring described in Comm. XXI is not used in the present paper; b) Comm. X, *Monat Chem.*, **83**, 394 (1952) and Comm. XXII, *Zeit. Naturforschung*, **8b**, 000 (1953); c) Comm. XXIII, ibid. **8b**, 000 (1953): d) Comm. XXV, ibid., **8b**, 161 (1953); e) Comm. XXVII, *Monat. Chem.*, **84**, 512 (1953); f) Comm., III and IV, *Zeit. Naturforschung*, **5b**, 307 (1950) and **6b**, 48 (1951).

[4] As for $\eta$-BHC of the configuration of e.e.p.e.p.p. compare: R. Riemschneider, Komm., XXIV, *Monat. Chem.* **84**, 000 (1953).

vellous power as an insecticide.

Thus the determination of the geometrical configuration of the isomers of these compounds is most desirable, but it usually requires much time. As the halogen-carbon bond has a large dipole moment, its measurement would afford an effective means for this purpose, as in the case of the isomers of BHC.5)

The critical discussions of the structure of the compounds stated here have already been presented elsewhere by one of the present authors (R.R.)[3b-f], also taking into account the dipole moment. The aim of this paper is to report the details of the measurement as well as the full information of the calculation.

## Experimental

**Materials** All the samples measured had been prepared by one of the present authors (R.R.)[3b-f] and their dipole moments were measured by another (I. M.) without further purification.

The solvent benzene was made free from thiophene by aluminium chloride, dried over metallic sodium and then distilled, the fraction boiled within 0.1°C being collected for use.

**Measurement** The density $d$ and dielectric constant $\varepsilon$ of the solution in benzene were measured with a pycnometer and a heterodyne beat apparatus in a manner previously described.5) The wavelength used was about 150 meters. The polarization $p_{2\infty}$ of the solute was calculated by the following formula derived by Halverstadt-Kumler's method6):

$$p_{2\infty}=\frac{\varepsilon_1-1}{\varepsilon_1+2}\,\frac{1}{d_1}\left[1+\frac{3a}{(\varepsilon_1-1)(\varepsilon_1+2)}-\frac{b}{d_1}\right] \tag{1}$$

where $\varepsilon_1$, and $d_1$ are respectively the dielectric constant and density of the solvent, and $a$ and $b$ are the coefficients of the linear expansion of dielectric constant and density of the solution with respect to the weight fraction $w$:

$$\varepsilon=\varepsilon_1+aw, \tag{2}$$

and

$$d=d_1+bw. \tag{3}$$

Then the dipole moment $\mu$ is given by the equation:

$$\mu=0.0128\left[(P_{2\infty}-P_{\mathrm{E}}-P_{\mathrm{A}})\,T\right]^{1/2}, \tag{4}$$

where $P_{2\infty}=M_2p_{2\infty}$ is the molecular polarization, ($M_2$ being the molecular weight), $P_{\mathrm{E}}$ and $P_{\mathrm{A}}$ are the electronic and atomic polarization of the solute respectively. $P_{\mathrm{E}}$ was taken to be equal to the molar refraction $MR_{\mathrm{D}}$ for sodium D line, which was calculated by the use of the atomic refraction given in "Landolt-Börnstein Tabellen" and $P_{\mathrm{A}}$ was assumed to be 5 percent of $MR_{\mathrm{D}}$.

The temperature of the thermostat was kept all through at 30°C, because at the time when this measurement was undertaken the room temperature sometimes exceeded 25°C.

## Results

The weight fraction of the solute, $w$, the dielectric constant, $\varepsilon$ and the density, $d$, of the solution are given in Table I, together with the coefficients $a$ and $b$ calculated from them. The molecular polarization, $P_{2\infty}$, and the dipole moment $\mu$ thus obtained are listed in Table II.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AT 30°C

| $w$ | $\varepsilon$ | $d$ |
|---|---|---|
| 1. Tetrabromodichlorocyclohexane, $C_6H_6Cl_2Br_4$, m. p. 203°. | | |
| 0.00000 | 2.2615 | 0.8685 |
| 0.01814 | 2.2823 | 0.8789 |
| 0.02971 | 2.2947 | 0.8865 |
| | $a=1.11_9$ | $b=0.603$ |
| 2. Dibromotetrachlorocyclohexane, $C_6H_6Cl_4Br_2$, m. p. 178°. | | |
| 0·00105 | 2.2738 | 0.8742 |
| 0.01937 | 2.2846 | 0.8792 |
| 0.03143 | 2.3007 | 0.8862 |
| 0.04298 | 2.3142 | 0.8923 |
| | $a=1.22_6$ | $b=0.555$ |
| 3. Dibromotetrachlorocyclohexane, $C_6H_6Cl_4Br_2$, m. p. 285°. | | |
| 0.01092 | 2.2632 | 0.8738 |
| 0.01894 | 2.2644 | 0.8777 |
| | $a=0.153$ | $b=0.487$ |
| 4. Decachlorocyclohexene, $C_6Cl_{10}$, m. p. 95°. | | |
| 0.01464 | 2.2646 | 0.8755 |
| 0.02455 | 2.2668 | 0.8809 |
| 0.03551 | 2.2692 | 0.8865 |
| 0.05274 | 2.2728 | 0.8955 |
| | $a=0.214$ | $b=0.511$ |
| 5. Octachlorocyclohexane, $C_6H_4Cl_8$, m. p. 93°. | | |
| 0.01328 | 2.2755 | 0.8742 |
| 0.02259 | 2.2858 | 0.8791 |
| 0.04094 | 2.3053 | 0.8879 |
| 0.06166 | 2.3274 | 0.8983 |
| | $a=1.069$ | $b=0.475$ |
| 6. $C_6H_5O_2Cl$, m. p. 123-124° | | |
| 0.01371 | 2.3661 | 0.8724 |
| 0.02393 | 2.4425 | 0.8762 |
| 0.03737 | 2.5404 | 0.8809 |
| 0.05014 | 2.6324 | 0.8856 |
| | $a=7.39_7$ | $b=0.359$ |
| 7. 2, 2, 6, 6,-Tetrachlorocyclohexanone, $C_6H_6OCl_4$, m. p. 84°. | | |
| 0.01371 | 2.3757 | 0.8737 |
| 0.02772 | 2.4980 | 0.8789 |
| 0.04252 | 2.6300 | 0.8846 |
| 0.05905 | 2.7803 | 0.8910 |
| | $a=8.98_1$ | $b=0.381$ |

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5) Y. Morino, I. Miyagawa, and T. Oiwa, *Botyu-kagaku*, **15**, 181 (1950).

6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

8. 1,4-Dichlorocyclohexadiene-(1,4), $C_6H_6Cl_2$, m. p. 63°.

| | | |
|---|---|---|
| 0.03516 | 2.2661 | 0.8778 |
| 0.05975 | 2.2694 | 0.8844 |
| | $a=0.132$ | $b=0.265$ |

TABLE II

MOLECULAR, ELECTRONIC, AND ATOMIC POLARISATIONS, AND DIPOLE MOMENTS AT 30°C

| Compounds | m.p. | $P_{2\infty}$(cc) | $P_E+P_A$ (cc) | $\mu$(D) |
|---|---|---|---|---|
| Tetrabromodichloro-cyclohexane | 203 | 148.0 | 71.9 | 1.93 |
| Dibromotetrachloro-cyclohexane | 178 | 135.4 | 65.8 | 1.84 |
| Dibromotetrachloro-cyclohexane | 285 | 67.8 | 65.8 | 0.3 |
| Decachlorocyclo-hexene | 95 | 77.2 | 75.9-79.9 | 0. |
| Octachlorocyclo-hexane | 93 | 128.8 | 70.0 | 1.69 |
| $C_6H_5O_2Cl$ | 123-124 | 236 | 34.2 | 3.14 |
| 2,2,6,6-Tetrachloro-cyclohexanone | 84 | 451 | 50.0 | 4.40 |
| 1,4-Dichlorocyclo-hexadiene-(1,4) | 63 | 39.1 | 37.2 | 0.3 |

1. **Tetrabromodichlorocyclohexane $C_6H_6Cl_2Br_4$ m. p. 203° and Dibromotetrachlorocyclohexanes, $C_6H_6Cl_4Br_2$ m. p. 178° and 285°.** Judging from the method of preparation of these compounds, there is no doubt that they are 1, 2, 3, 4, 5, 6-substituted ones,[3b-c] exactly similar to BHC, though the accurate positions of the bromine atoms are not definitely assigned. The spacial configurations of the six isomers of BHC are schematically shown in Fig. 1, where the cyclohexane ring is represented by a hexagonal ring, the chlorine atom in an equatorial bond (e-bond) by a short line, the chlorine atom in a polar bond (p-bond) by a small circle on the hexagonal ring, the white and black circles denoting chlorine atoms above and below the central plane.

Now the moments of these compounds are considered to be nearly the same as, or slightly smaller than, those of the corresponding isomers of BHC, since the bond moment of the C–Br bond is nearly the same as that of the C–Cl bond. The moments of the isomers of BHC were found to be $\alpha$: 2.2 D, $\beta$: 0 D, $\gamma$: 2.8 D, $\delta$: 2.2 D, and $\varepsilon$: 0 D. The moment of $\eta$-isomer has not been measured, but according to the rule suggested by Y. Morino, I. Miyagawa, and T. Oiwa,[5] it is estimated to be 1.88 D. Therefore, the observed values of the dipole moments of $C_6H_6Cl_2Br_4$, m. p. 203° (1.93 D) and of $C_6H_6Cl_4Br_2$, m.p. 178° (1.84 D) apparently indicate that they are neither $\beta$ nor $\varepsilon$, but $\alpha$, $\delta$ or $\eta$ type compounds. The $\eta$-form may be safely eliminated from our consideration, because the abundance of the corresponding chlorine compound is extremely small. It can not be discriminated, however, whether they are of $\alpha$-type or of $\delta$-one.

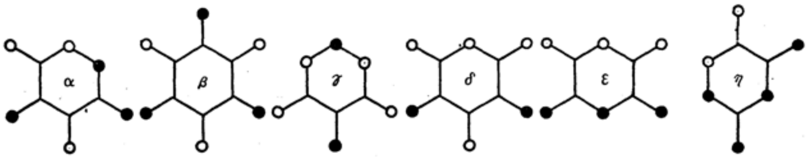
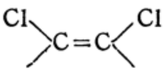
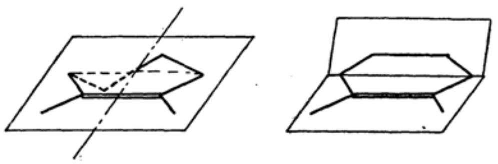


Fig. 1. Configuration of the Isomers of BHC.

Similarly it is concluded that $C_6H_6Cl_4Br_2$, m.p. 285° is of $\beta$ type or of $\varepsilon$ one, since its moment is negligibly small. Considering the fact that its melting point is as high as that of the $\beta$-isomer of BHC (310°), it seems probable that $C_6H_6Cl_4Br_2$, m.p. 285° has the configuration of $\beta$-form.

2. **Decachlorocyclohexene, $C_6Cl_{10}$.** For the cyclohexene ring two forms should be considered: first, the $C_2$ form corresponding to the chair form of the cyclohexane ring, and second, the $C_s$ form corresponding to the boat form (See Fig. 2). The dipole moments for both forms are calculated to see which form is actually realized in this case. The assumptions used are as follows: the moment of the group  $\mathrm{Cl}\!>\!C{=}C\!<\!\mathrm{Cl}$ is 1.74 D, located in the plane ClC=CCl and perpendicular to the double bond. The moments of the C–Cl bonds attached to other carbon atoms are 1.86 D. At the same time the induction effect suggested by us[5] are taken into account it is assumed that the C–Cl bond which is marked



$C_2$-form  $C_s$-form

Fig. 2. The two forms Cychohexene Ring

by a circle in Fig. 3, induces at each bond in the direction along the bond the moment shown in the figure, the moments induced perpendicularly to the bonds being all disregarded. Of course this rule is an empirical one, but it has served to enable us to compute with reasonable accuracy not only the moments of fourteen chlorinated aliphatic hydrocarbons but also those of eleven compounds which have a cyclohexane ring.

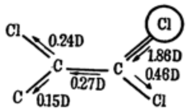


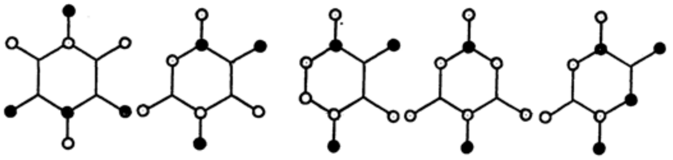
Fig. 3. The Induction Moments due to C–Cl Dipole

The calculated values of the dipole moments by use of these assumptions are found to be 0.40 D for $C_s$ form and 0.14 D for $C_2$ form. Both of them lie in the allowed region from the observed value 0D, so that the configuration of the cyclohexene ring can not be decided by this discussion.

Though the present calculation gave no discrimination between the two forms, it has the merit of providing a strong evidence that in the vector addition for computing the dipole moment of a molecule, the induction effect can by no means be put out of the consideration, because, otherwise, it will result in values larger even than 2D for decachlorocyclohexene, in sharp contrast to the observed zero moment.

3. **Octachlorocyclohexane, $C_6H_4Cl_8$, m.p. 93°.** The sample was prepared by the chlorination of *p*-dichlorobenzene.[3e] It is evident that it is 1,1,2,3,4,4,5,6-substituted compound, so that the geometrical configuration of this compound must be one of the following five forms:

| | | |
|---|---|---|
| (1) | (1pe, 2e, 3e, 4pe, 5e, 6e) | 0 D |
| (2) | (1pe, 2p, 3e, 4pe, 5e, 6e) | 1.47 D |
| (3) | (1pe, 2p, 3p, 4pe, 5e, 6e) | 1.86 D |
| (4) | (1pe, 2p, 3e, 4pe, 5e, 6p) | 1.93 D |
| (5) | (1pe, 2p, 3e, 4pe, 5p, 6e) | 0 D |



(1) (2) (3) (4) (5)

Fig. 4. The Configurations of the Isomers of Octachlorocyclohexane

Their spacial configurations are illustrated in Fig. 4. The computed moments of these isomers are also given in the above, the assumptions for the calculation being the same as those used in the preceding case. The observed value, 1.69 D, suggests that it is neither (1) nor (5), but one of (2), (3), and (4). It cannot be confirmed which one of them should be assigned to $C_6H_4Cl_8$, m.p. 93°, but the most stable form (2) may be the most favourable. The reason is that the form (2) has one pair of polar C–Cl bonds, while the form (3) has two pairs and the form (4) three pairs of them. The most important part of the intramolecular potential energy of this molecule may be due to the steric repulsion between this pair of polar C–Cl bonds, which project toward the same direction at a very close proximity. The difference 0.22 D between the calculated and the observed may be ascribed to the rough approximation of the calculation.

4. **Tetrachlorocyclohexanone, $C_6H_6OCl_4$.** It was prepared by the chlorination of cyclohexanol, and the substitution by chlorine atoms was confirmed to take place at 2,2,6,6-positions.[3d] In order to estimate the dipole moment of this molecule, some additional assumptions are necessary for the value of C=O moment itself and the induction effect due to C=O bond, besides the induced moments by C–Cl bond shown in Fig. 3. The C=O bond moment may be taken to be 2.80 D from the moment of cyclohexanone.[8] If we tentatively assume for the induction effect upon and by the C=O bond the same amounts as those of the C–Cl bond, then 3.78 D is obtained for the total moment of this molecule.* The discrepancy between this and the observed value, 4.40 D, should, of course, be attributed to the provisional assumptions for the induced moment. In fact, larger induced moments should be assigned to them, since the bond moment of C=O is larger than that of the C–Cl bond. If the moments induced by the C=O dipole are increased by the ratio 2.80 / 1.86,** (Fig. 5 shows the individual values of the induced moments in this case), the computed values of the moment of this molecule becomes 4.21 D.

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[8] J. W. Williams *J. Am. Chem. Soc.* **52** 1831 (1930).

* The valency angles are all assumed to be tetrahedral.

** The moment induced at the C=O bond C-Cl bond remains 0.24 D, the same as that at the C-Cl bond.

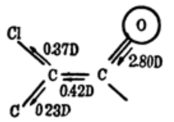
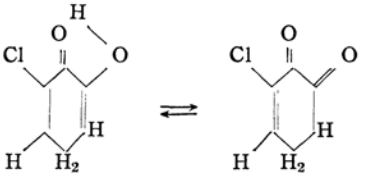


Fig. 5. The Induction Moments due to C=O Dipole

**5. $C_6H_5O_2Cl$, m.p. 123-124° from 2,2,6,6-Tetrachlorocyclohexanone.**[3d] It has been found that this compound has the following two tautomers in equilibrium in the ratio of I>II.[3d]



I II

(I>II)

In order to make sure of this conclusion, the moments of the two forms (I) and (II) are calculated by the ordinary assumptions that C–Cl : 1.60 D, C–O : 1.10 D, C=O : 2.80 D, O–H: 1.53D, ∠HOC : 100°, and the bonds C–Cl, C=O, and O–H are all located in one plane,* and that the induced moments are the same as those of 2,2,6,6-tetrachlorocyclohexanone, which gave 3.78 D for its moment. The calculated moment of the form I is 1.98 D, and that of the form II is 4.33 D.** Thus, in order to explain the observed moment 3.14 D, it must be assumed that the forms I and II coexist in equilibrium at the ratio of 60 % to 40 %. Needless to say, no great credit should be laid to the value of this ratio,*** since the moments of the two forms used for the calculation are based upon many hypothetical assumptions. Yet it is enough to support the conclusion stated above that this compound is a tautomeric mixiure of the two forms, form I predominating.

6. **1,4-Dichlorocyclohexadiene-(1,4).**[3f] Since the four bonds attached to the ethylenic carbon atoms are located in one plane, this molecule has to be folded by the axis through the central two carbon atoms. If the angle ∠C=C–Cl be denoted by $\theta$, and the angle between the two planes by $\varphi$ (See Fig. 6), then the resultant moment is simply given by

$$\mu=2\mu_{ccl}\sin\theta\sin\frac{1}{2}(\pi-\varphi)$$

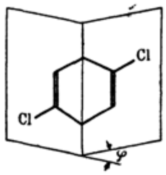


Fig. 6. The Configuration of 1,4-Dichlorocyclohexadiene-(1,4)

Therefore, inserting the value of $\mu=0.30$ D, together with $\mu_{ccl}=1.60$ D, and $\theta=120°$, we get $\varphi=14°$.

On the other hand, if we assume the angle of ∠C=C–C to be 120°, and the angle of ∠C–C–C of the central carbon atoms to be tetrahedral, then the angle between the two planes is geometrically obtained to be 40°. At a glance, it seems that there exists a serious difference between the calculated and the observed, but, if some allowance be made for the valency angles, the observed value of $\varphi$ stated above can be brought into the allowed region of the molecular model. For instance, the application of the the angles ∠C=C–C: 123°, and ∠C–C–C: 112°, gives $\varphi=17°$ instead of 40°. In fact, the widening of the valency angle are readily acceptable if we consider the fact that the repulsion between the nonbonded carbon atoms has the possibility of making the valency angles wider by a few degrees.

Here it should be noted that the values of $\varphi$ computed from the dipole moment may have some errors, because the observed moment is so small that the values obtained for the angle are greatly affected by the assumption employed for the atomic polarisation. If we take $P_E+P_A=MR_D$ in place of 1.05 $MR_D$, the moment will increase to 0.42 D, resulting in the increase of the angle to 20°. Thus it can be concluded that the cyclohexadiene-(1,4) ring is folded, but flatter than expected by an ordinary tetrahedral angle.

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* It can be easily shown that the actual deviation from the plane is virtually small.

** The interaction of two double bonds in the conjugated position is not considered for the time being.

*** The complete neglect of the induction effect provides 2.65 D and 5.11 D for the moment of the two forms, resulting in 85% to their concentrations.