

The Dipole Moments of the Isomers of Benzene Hexachloride and its Related Compounds. Yonezo MORINO, Ichiro MIYAGAWA and Toshihiko ORWA (Chemical Laboratory, Faculty of Science, Tokyo University and Takei Laboratory, Institute for Chemical Research, Kyoto University) Received Aug. 28, 1950. *Botyu-Kagaku* 15, 181 (1950)

30. BHC 異性体及びその近縁物質の双極子能率に就いて 森野米三, 宮川一郎, 大岩俊彦  
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BHC 及びその近縁物質の構造決定は著者の一人<sup>1,18)</sup> によつて有機化学的立場から行はれている。これと並行して物理化学的立場から安定状態にある分子を直接に観察することは必要な事と考えられる。我々は今回双極子能率の面から此等の物質の分子構造の検討を行つた。

25°, benzene 溶液に於ける測定の結果は Table I 及び II に示すようである。

さて双極子能率によつて分子構造を明かにする爲には先ず考えられるすべての分子模型に就いて能率を計算しなくてはならない。然し乍ら BHC 及びその近縁物質では同一分子内に極性の大きい C-Cl 基が多数含まれている爲にそれ等の間の相互作用を無視する事はできない。従つて普通行われているような單なる基能率の vector addition として計算するのでは不十分である。この爲に我々は一般に炭化水素の塩素誘導体の双極子能率を計算する爲の一つの通則を呈出した。Table III に明かであるように炭化水素の種々の塩化物に就いてこの通則によつて求めた計算値は実験値とよく一致する。依つて目的とする BHC 及びその近縁物質の計算値の算出は此の通則によつて行つた。

Cyclohexane 環を椅子型とすると<sup>10)</sup> BHC, hepta 及び octa で考えられる幾何異性体の数は夫々 13, 20 及び 29 となり Fig. 1, Fig. 2 及び Fig. 3 に示すようである。図中の数字は上述の方法で計算した双極子能率を示す。同一番号中 dash (') を附したものと然らざるものがあるが両者は cyclohexane 環を裏返すことによつて移り変わり得るものであり、しかもこの転移は cyclohexane の他の誘導体の場合から<sup>11)</sup> 類推すれば自由に起り得ると想像される。Cyclohexane 環に於いて一つおきの炭素原子の p-bond に結合した塩素原子間距離 (例えば  $I_6$  では此のような対が 6 つある) は炭素原子を正四面体と考えるとき 2.52 Å で Cl-Cl の van der Waals 距離 3.60 Å に比して極めて近く、Cl-Cl 間に大きい斥力が作用する。従つて dash (') のついた番号の異性体は今一つの異性体に比して energy が非常に高く実際問題としてその存在を考慮する必要がない。かくして考えるべき分子型は dash (') の無いものとなり、その数は夫々 8, 10 及び 17 となる。

BHC 中  $\gamma$ -異性体の能率 2.90 D を与えるものは  $VI_6$  (2.93 D) のみであるから此れが  $\gamma$ -異性体の構造である。 $\alpha$ -及び  $\delta$ -異性体の能率 2.22 D を与えるものは  $II_6$  (2.25 D) と  $III_6$  (2.25 D) の二つであるが、 $\alpha$ -異性体には光学的異性体が存在するから<sup>15)</sup>  $III_6$  が  $\alpha$ -異性体の構造であり、 $II_6$  が  $\delta$ -異性体の構造である。 $\beta$ -及び  $\epsilon$ -異性体の能率は 0 であるが、これ等に相当する構造は  $I_6$  と  $V_6$  である。然し乍ら  $\beta$ -異性体の構造が  $I_6$  であることは既に X-線解析によつて決定されているから<sup>16)</sup>  $V_6$  が  $\epsilon$ -異性体の構造である。以上の結果は Vloten 等<sup>13)</sup> が  $\gamma$ -異性体で X-線解析から得た結果、Bastiansen 等<sup>17)</sup> が電子線廻折から得た結果及び大岩等<sup>1)</sup> が有機化学的に得た結果と一致する。

$\alpha$ - 及び  $\gamma$ -hepta の能率 1.19 D 及び 1.35 D に近い計算値を与えるものは  $I_7$  (1.02 D),  $II_7$  (1.25 D),  $IV_7$  (1.45 D) 及び  $VII_7$  (0.85 D) である。大岩等の有機化学的研究によると  $\alpha$ - 及び  $\gamma$ -hepta の構造は夫々  $I_7$  及び  $II_7$  であり、我々の能率の値は此れを支持する。又  $\delta$ - 及び  $\epsilon$ -hepta の能率 2.20 D に近い計算値を与えるものは  $V_7$  (2.23 D),  $VI_7$  (2.37 D),  $VIII_7$  (1.97 D) 及び  $IX_7$  (2.20 D) であるが、 $\delta$ -hepta と  $\epsilon$ -hepta の実測値が殆んど等しいと云ふ点からこれ等の構造は  $V_7$  か  $IV_7$  となる。此の結果は中島等<sup>7)</sup> の  $\gamma$ -BHC の脱塩酸及び塩素化反応及び大岩等<sup>18)</sup> の塩素化反応の結論を支持する。

$o$ - 及び  $\beta$ -p-octa は非常に小さい能率を持ちこれ等に相当する構造は  $I_8$ ,  $III_8$ ,  $XVII_8$  及び  $XIII_8$  である。然し乍ら後二者は上述した大きな斥力を有する Cl-Cl の対を二つも有つことから合成の際生成する確率は前二者に比して小さいと考えられる事及び  $o$ - 及び  $\beta$ -p-octa が夫々  $o$ - 及び p-dichlorobenzene の塩素化によつて得られる事からそれ等の構造は夫々  $I_8$  及び  $III_8$  となる。これも大岩等<sup>1)</sup> の結果と一致する。

終りに種々研究上の便宜を与えられた武居三吉教授、大野稔博士、 $\epsilon$ -BHC の試料を提供された Dow Chem. Co. の K. C. Kauer 博士、 $\delta$ -hepta の試料を提供された中島稔助教授及びこの研究中種々援助を与えられた末高治並びに山田良一両氏に謝意を表す。又研究費の一部は文部省科学研究費に仰いだ。

The structures of the isomers of BHC and its related compounds have been determined from the standpoint of chemical reactions by one of the present authors<sup>1,7,18</sup>, but it is also desirable to study the geometrical configuration of the stable molecules by the measurement of dipole moment. Although there are several measurements on the dipole moments of the isomers of BHC by E. Hetland<sup>2</sup>, S. K. K. Jatkar and S. B. Kurkarni<sup>3</sup>, M. Rolla, P. Fontana and A. M. Marinangeli<sup>4</sup>, Y. Morino, I. Miyagawa, H. Shio and S. Nagakura<sup>5</sup>, and other authors<sup>6</sup>, their observed values do not agree with each other in some cases, and they are far from the values calculated by simple vector addition of the bond moments. So on the one hand we have measured the dipole moments of all the isomers of BHC using the most pure samples we obtained, as well as some isomers of monochlorobenzene hexachloride (hepta) and of dichlorobenzene hexachloride (octa), and on the other hand we have made some trials for computing the moments which these isomers should have.

### Experimental

**1. Materials:** The solvent benzene was made free from thiophene by aluminium chloride. It was then dried over metallic sodium and distilled; the fraction boiled within 0.1°C was collected for use.

All the samples of BHC, hepta and octa except  $\delta$ -hepta were the same as those used by Oiwa<sup>1,18</sup> in his chemical studies. Their purity was confirmed by melting points, half wave potentials and chlorine contents. The  $\delta$ -hepta used was given by M. Nakazima, which was prepared from  $\gamma$ -BHC by dehydrochlorination and then chlorination<sup>7</sup>.

**2. Measurement:** The density  $d$  and the dielectric constant  $\epsilon$  of the solution in benzene were measured with a pycnometer and a heterodyne beat apparatus in a manner previously described<sup>8</sup>. The wave length used is about 150 meters. The molar polarization  $P_2$  of the solute was calculated by means of the following Debye equation:

$$p_{12} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d} \quad (1)$$

and

$$P_2 = M_2 \left( \frac{p_{12} - p_1}{w} + p_1 \right) \quad (2)$$

in which  $P_{12}$  is the polarization of solution,  $w$  is the weight fraction of solute,  $M_2$  the molecular weight of solute. The extrapolation of  $P_2 \sim w$  curve to infinite dilution gives the values  $P_{2\infty}$  at the temperature  $T$ , from which the dipole moment  $\mu$  is calculated by the equation:  $\mu = 0.0127\sqrt{(P_{2\infty} - P_E - P_A)T}$  (in Debye unit) (3) where  $P_E$  and  $P_A$  are the electronic and atomic polarization respectively.  $P_E$  was taken to be equal to the molar refraction  $MR_D$  for D sodium line, which was calculated by atomic refraction given in "Landolt-Börnstein Tabellen" and  $P_A$  was assumed to be 5% of  $MR_D$ . The reliability of this assumption was confirmed by the values of  $P_{2\infty}$  of  $\beta$ - and  $\epsilon$ -BHC,  $\beta$ -p-octa and o-octa, which were almost coincident with the values of  $P_E + P_A$  thus estimated.

### Results

The weight fractions,  $w$ , of the solute, the dielectric constants,  $\epsilon$ , the densities,  $d$ , and the molar polarization,  $P_2$ , are given in Table I. The molar refractions  $MR_D$ , the electronic and atomic polarizations,  $P_E + P_A$ , calculated from molar refractions as stated above, the polarizations  $P_{2\infty}$  obtained by extrapolation to infinite dilution, and the dipole moments  $\mu$  are given in Table II.

Table I. Dielectric Constants and Densities of Benzene Solutions and Polarizations,  $P_2$  at 25°C.

$w$	$\epsilon$	$d$ (g/cm <sup>3</sup> )	$P_2$ (c.c.)
$\alpha$ -BHC			
0.00000	2.2720	0.87041	
0.01015	2.2914	0.87462	156.0
0.02009	2.3111	0.87872	157.6
0.03866	2.3454	0.88680	152.5
0.05622	2.3785	0.89525	149.0
$\beta$ -BHC			
0.01148	2.2736	0.87524	59.8
0.01589	2.2742	0.87717	58.7
$\gamma$ -BHC			
0.01572	2.3218	0.87809	219.6
0.02821	2.3628	0.88367	219.8
0.04849	2.4284	0.89250	216.9
0.07749	2.5268	0.90638	213.1
$\delta$ -BHC			
0.00993	2.2926	0.87479	162.0
0.01958	2.3118	0.87891	159.1
0.03696	2.3475	0.88645	159.0
0.06020	2.3590	0.89677	156.7

$\epsilon$ -BHC			
0.01674	2.2753	0.87776	60.5
0.02573	2.2772	0.88202	59.6
0.03265	2.2790	0.88522	60.2
0.04232	2.2804	0.88946	59.9
$\alpha$ -hepta			
0.01117	2.2803	0.87587	94.3
0.02217	2.2869	0.88049	94.3
0.03896	2.2979	0.88762	95.7
0.05974	2.3114	0.89740	94.3
$\gamma$ -hepta			
0.01900	2.2870	0.87897	102.5
0.02936	2.2960	0.88392	102.8
0.04643	2.3095	0.89148	102.6
0.06515	2.3246	0.89985	102.8
$\delta$ -hepta			
0.01004	2.2893	0.87472	164.2
0.02076	2.3094	0.87958	163.3
0.03976	2.3440	0.88828	162.7
0.06102	2.3874	0.89918	162.0
$e$ -hepta			
0.01749	2.3039	0.87838	163.5
0.02598	2.3181	0.88225	159.8
0.04289	2.3473	0.89025	156.7
0.05888	2.3730	0.89751	153.7
$\beta$ -p-octa (from monochlorobenzene)			
0.00901	2.2735	0.87430	73.4
0.01146	2.2739	0.87530	75.2
$\beta$ -p-octa (from $\beta$ -BHC)			
0.00801	2.2732	0.87382	73.2
0.01095	2.2744	0.87535	73.4
$\beta$ -p-octa (from p-dichlorobenzene)			
0.00990	2.2730	0.87456	73.6
0.01116	2.2736	0.87520	72.6
o-octa (from o-dichlorobenzene)			
0.01920	2.2751	0.87893	71.9
0.03202	2.2782	0.88445	74.8
0.05041	2.2817	0.89284	74.1
0.07953	2.2865	0.90586	74.1
o-octa (from $\beta$ -BHC)			
0.01953	2.2777	0.88001	73.7
0.03027	2.2793	0.88462	73.7
0.04243	2.2810	0.89032	72.4
0.05739	2.2836	0.89667	73.4

The values of the moments of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -BHC agree well with our previous measurements<sup>9</sup> and with those of E. Hetland<sup>10</sup>. The values of  $\alpha$ - and  $\gamma$ -hepta are of almost the same order of magnitude, but, strictly speaking, that of the former is smaller than the latter.  $\delta$ - and  $e$ -hepta have quite the same value of 2.20 D. The  $\beta$ -p-octas obtained from three different starting materials (monochlorobenzene,  $\beta$ -BHC

Table II. Molar Refractions,  $MR_D$ , Polarizations,  $PE+PA$ ,  $P_{2\infty}$  and Dipole Moments.

Compounds	m. p. (°C)	$P_{2\infty}$ (c.c.)	$MR_D$ (c.c.)	$PE+PA$ (c.c.)	$\mu$ (D)
$\alpha$ -BHC	157~158	162	57	60	2.22
$\beta$ -BHC	310	69	57	60	0
$\gamma$ -BHC	111~112.5	223	57	60	2.80
$\delta$ -BHC	138~139	163	57	60	2.22
$e$ -BHC	212~215	60	57	60	0
$\alpha$ -hepta	153~154	94	62	65	1.19
$\gamma$ -hepta	84~85	103	62	65	1.35
$\delta$ -hepta	139~140	165	62	65	2.20
$e$ -hepta	55~55.5	165	62	65	2.20
$\beta$ -p-octa (from monochlorobenzene)	265~266	74	67	70	0.44
$\beta$ -p-octa (from $\beta$ -BHC)	265~266	73	67	70	0.40
$\beta$ -p-octa (from p-dichlorobenzene)	265~266	73	67	70	0.40
o-octa from o-dichlorobenzene)	150~150.5	74	67	70	0.44
o-octa (from $\beta$ -BHC)	149.5~150	73	67	70	0.40

and p-dichlorobenzene) have the same value of 0.40~0.44 D, which not only give us a confidence in this value, but also confirm that these substances are the same. Quite the same thing is true about o-octa's, which were obtained by chlorination of  $\beta$ -BHC and of o-dichlorobenzene.

### Discussion of Results

#### 1. An Empirical Rule for Calculating the Dipole Moments of Chlorinated Hydrocarbons.

In order to study the molecular structure from dipole moment data, it is necessary to calculate the moments for several assumed structures and compare those with the experimental values. The ordinary method of calculation is a simple vector addition of each bond moment, but some corrections are necessary to obtain reliable results as we can not neglect several factors such as induction effect. These corrections might be very large in such a molecule as those of BHC and its related compounds, which have several C-Cl bonds in very close positions. There are a number of reports<sup>11</sup> on the theory of these corrections but they can not provide us

with conclusive results because many unspecified parameters are necessary for their application. Here we propose a simple rule for the calculation of the moment of chlorine substituted hydrocarbons\* as follows:

1) C-Cl bond and C-H bond are assumed to have the original moments of 1.86 D\*\* and 0.00 D\*\*\* respectively.

2) In C-Cl bond whose C atom is in the  $\alpha$ -position to the first Cl atom, a moment of 0.46D is induced+ in the direction of C $\rightarrow$ Cl.

Table III. The Comparison of the Observed and the Calculated Dipole Moments of Chlorinated Hydrocarbons.

Compounds	Dipole Moments (D)		
	Obs. (in the gaseous State)	Calcd. by our Rule	Calcd. by simple vector Addition
CH <sub>3</sub> Cl	1.86 a	1.86	1.86
CH <sub>2</sub> Cl <sub>2</sub>	1.62 b	1.62	2.15
CHCl <sub>3</sub>	0.95 <sup>c</sup>	0.94	1.86
C <sub>2</sub> H <sub>5</sub> Cl	2.02 a	1.97	1.86
n-C <sub>3</sub> H <sub>7</sub> Cl	2.04 a	2.12	1.86
n-C <sub>4</sub> H <sub>9</sub> Cl	2.11 d	2.12	1.86
(CH <sub>3</sub> ) <sub>2</sub> CHCl	2.15 d	2.06	1.86
(CH <sub>3</sub> ) <sub>3</sub> CCl	2.13 e	2.13	1.86
CH <sub>3</sub> CHCl <sub>2</sub>	2.05 f	1.97	2.15
CH <sub>3</sub> CCl <sub>3</sub>	1.77 e	1.75	1.86
CH <sub>2</sub> ClCCl <sub>3</sub>	1.39 g	1.38	2.15
CHCl <sub>2</sub> CCl <sub>3</sub>	0.92 g	0.86	1.86
Chlorocyclohexane	2.30 h		
(Benzene)		2.36	1.86
CH <sub>2</sub> ClCH <sub>2</sub> Cl (gauche)	2.67 i	2.64	3.03

- a) Sanger, R., Steiger, O. and Gachter, K.: *Helv. phys. Acta*, **5**, 200 (1932).  
 b) Mahanti, P. C. and Sen-Gupta, D. N.: *J. Ind. Chem. Soc.*, **5**, 673 (1928).  
 c) Sanger, R.: *Physik. Z.*, **27**, 556 (1926).  
 d) Groves, L. G. and Sugden, S.: *J. Chem. Soc.*, p. 158 (1937).  
 e) Wiswall, R. II., Jr. and Smyth, C. P.: *J. Chem. Phys.*, **9**, 356 (1941).  
 f) Ghosh, P. N., Mahanti, P. C. and Sen-Gupta, D. N.: *Z. Physik*, **54**, 711 (1929).  
 g) Thomas, J. R. and Gwinn, W. D.: *J. Am. Chem. Soc.*, **71**, 2785 (1949).  
 h) Williams, J. W.: *J. Am. Chem. Soc.*, **52**, 1831 (1930).  
 i) Watanabe, I., Mizushima, S. and Morino, Y.: *Sci. Pap.*, I. P. C. R. **39**, 401 (1942).

3) In C-C bond whose C atom is in the  $\alpha$ -position to the first Cl atom, a moment of 0.27 D is induced in the direction of C $\leftarrow$ C.

4) In C-C bond whose C atom is in the  $\beta$ -position to the first Cl atom, a moment of 0.15 D is induced in the direction of C $\leftarrow$ C.

5) In C-Cl bond whose Cl atom is in the gauche++ position to the first Cl atom, a moment of 0.24 D is induced in the direction of C $\rightarrow$ Cl bond.

6) Bond angles are all assumed to be tetrahedral.

7) The vector sum of these moments gives the resultant moment of the complete molecule.

The resultant moments calculated by the above rule for several molecules are in good agreement with the observed as shown in Table III. In the following discussions we will use this rule throughout+++.

\* J. R. Thomas and W. D. Gwinn (*J. Am. Chem. Soc.*, **71**, 2785 (1949)) presented a semi-quantitative rule concerning the moments of the chlorinated methanes and ethanes.

\*\* This value is the observed moment of methylchloride in the gaseous state. cf: S. Sanger, O. Steiger and K. Gachter: *Helv. Phys. Acta*, **5**, 200 (1932).

\*\*\* If a finite value of C-H bond moment is used instead of 0.00 D, the moment of C-Cl bond should be diminished by the amount of C-H bond moment assumed. It can, however, easily be shown that the both methods provide quite the same result, as far as the bond angles are assumed to be regularly tetrahedral.

+ The term "induced" does not necessarily mean "induced electrostatically" in the classical sense.

++ It is concluded from the studies of the Raman effect and infrared spectra that ethylene dichloride consists of two rotational isomers; (a) the trans and (b) the gauche form. (Refer, for instances, S. Mizushima, Y. Morino, I. Watanabe and S. Yamaguchi: *J. Chem. Phys.*, **17**, 663 (1949)). The relative position of the two Cl atoms in (a) or (b) is said to be in the "trans" or the "gauche" position respectively.

+++ An extension of this rule to bromine and iodine substituted hydrocarbons is now being carried out and found to be hopeful. The results will be published elsewhere.

2. Geometrical Configuration of BHC, Hepta- and Octa-Chlorocyclohexane.

cluded from the electron diffraction investigation by O. Hassel et al.<sup>103</sup> that the cyclohexane

Fig. 1 Geometrical Configuration of the Isomers of BHC.

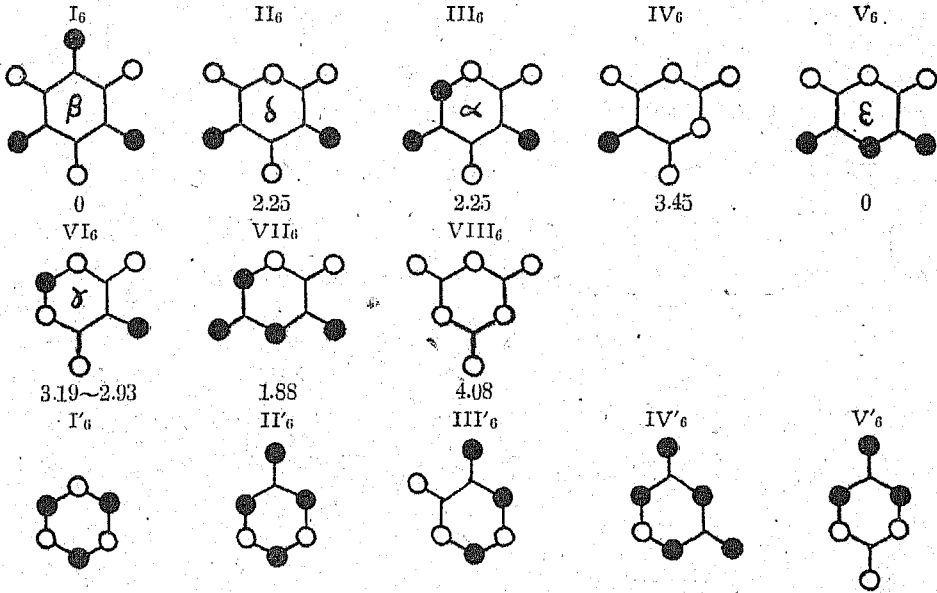


Fig. 2 Geometrical Configuration of the Isomers of Monochlorobenzene Hexachloride (Hepta).

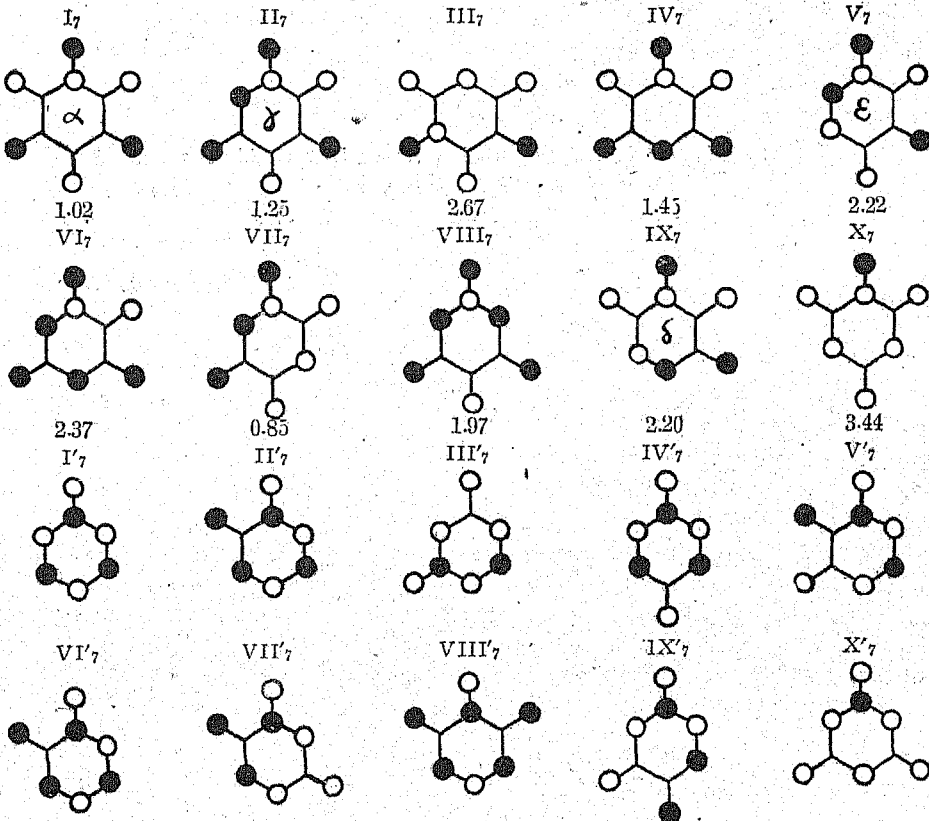


Fig. 3 a. Geometrical Configuration of the More Stable Isomers of Dichlorobenzene Hexachloride (Octa).

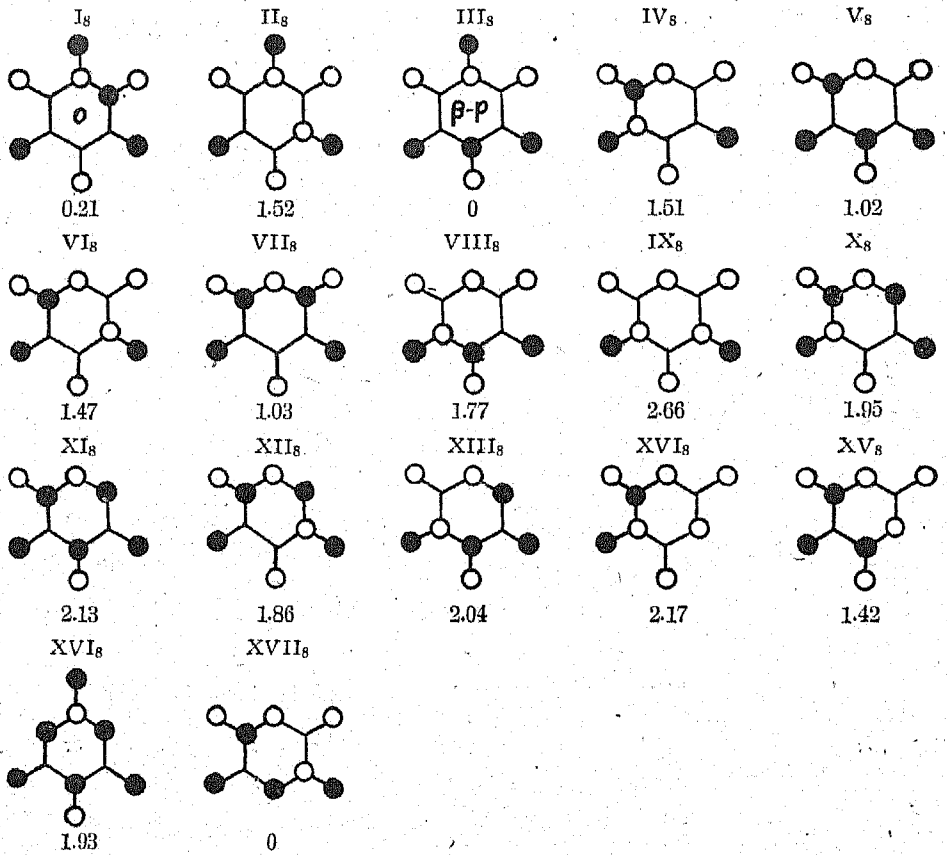
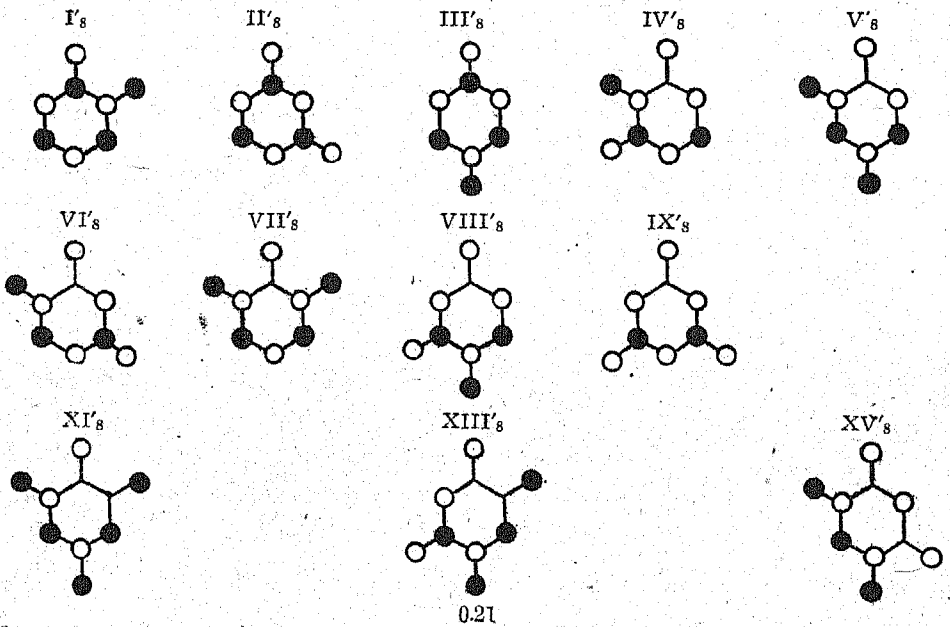


Fig. 3 b. Geometrical Configuration of the Less Stable Isomers of Dichlorobenzene Hexachloride (Octa).



ring has the chair form, it is also natural to conceive that the chlorine derivatives of cyclohexane should be of similar form. If we assume the chair form for cyclohexane ring, there exist 13, 20 and 29 geometrical isomers in BHC, hepta and octa, respectively. These are shown in Figs. 1, 2 and 3, together with their dipole moments computed by the rule stated above. In these figures the cyclohexane ring is represented by a hexagonal ring, chlorine atom in an equatorial bond (e-bond) by a short line, chlorine atom in a polar bond (p-bond) by a small circle on the hexagonal ring, and white and black circle represent chlorine atoms above and under the central plane.

On the other hand it was concluded from the Raman effect and dipole moment by Dr. K. Kojima<sup>11)</sup> that the cyclohexane ring can easily turn upside down in halogenated cyclohexane, resulting a ring of chair form with the equatorial and the polar bonds interchanged. The abundance ratio of the two isomers thus interchangeable by inversion, which we call "inverted isomers", is governed by the energy difference between the two forms. The same conclusion was also obtained by C. W. Beckett, K. S. Pitzer and R. Spitzer<sup>12)</sup> for dimethylcyclohexane.

In chlorinated cyclohexane the distance between the chlorine atoms in polar bonds which are bonded to the two alternate carbon atoms of cyclohexane ring is 2.52 Å, if the angles of the carbon valency bonds are fixed to be tetrahedral. This distance being very small compared with the Cl-Cl van der Waal's distance (3.60 Å), large repulsion between these chlorine atoms makes such a configuration unstable. The forms which are designated by dashes in Figs. 1, 2 and 3 (except XIII<sub>6</sub>) have more such pairs of chlorine atoms than another form of the inverted isomers, and therefore, are presumably very unstable and are negligible practically. The numbers of the isomers to be distinguished are thus reduced to 8, 10 and 17 for BHC hepta and octa respectively.

**3. Assignment of the Configuration to the Isomers of BHC.** In the first place, it can be easily seen from Fig. 1, that the structure which

should have the moment close to the observed (2.80D) of  $\gamma$ -BHC, is only VI<sub>6</sub>, which is the form concluded by G. W. van Vloten, Ch. A. Kruissink, B. Strijk and J. M. Bijvoet<sup>13)</sup> from x-ray diffraction measurement. The calculated value 3.19D is 0.4D larger than the observed and this difference is too large to be attributed to solvent effect. It is presumably due to the neglect of the induction effect between the two C-Cl polar bonds in parallel direction represented by white circles in VI<sub>6</sub> in Fig. 1. In fact, if this induced moment is assumed equal to that in the gauche position (0.24D), the moment of  $\gamma$ -BHC becomes 2.93D. We will use this assumption hereafter, which will be shown later to be legitimate for other cases.

The dipole moment of  $\delta$ -isomer has been reported to be zero by S. K. K. Jatar and S. B. Kurkarni<sup>14)</sup>, whereas to be 2.17D by E. Hetland<sup>15)</sup> and by E. Amble and O. Hassel<sup>16)</sup>. We obtained 2.22D for its value, which is quite the same as that of  $\alpha$ -isomer, 2.22D. The structures which have the moment close to this value are only the two forms of II<sub>6</sub> (2.25D) and III<sub>6</sub> (2.25D). Since  $\alpha$ -BHC have been separated to optical isomers by S. J. Cristol<sup>16)</sup> it should be assigned to III<sub>6</sub>, and consequently  $\delta$ -BHC to II<sub>6</sub>. The dipole moment of  $\epsilon$ -isomer was found to be zero in accord with the result by E. Hetland<sup>15)</sup>. The structures having the moment zero are I<sub>6</sub> and V<sub>6</sub>. The x-ray diffraction data<sup>16)</sup> indicated that the  $\beta$ -isomer has the structure of I<sub>6</sub>, and therefore,  $\epsilon$ -isomer must be V<sub>6</sub>. It seems to be interesting to state that the  $\beta$ -isomer which has a higher symmetry than  $\epsilon$ -isomer, has a higher melting point and lower solubility. The above conclusions concerning structures of five isomers of BHC agree completely with the result of the electron diffraction by O. Bastiansen,  $\phi$ . Ellefsen and O. Hassel<sup>17)</sup>.

**4. Assignment of the Configuration to the Isomers of Hepta.** The structures which have the moment approximately the same value as those of  $\alpha$ -hepta (1.19D) and  $\gamma$ -hepta (1.35D) are I<sub>7</sub> (1.02D), II<sub>7</sub> (1.25D), IV<sub>7</sub> (1.45D) and VII<sub>7</sub> (0.85D). It has been concluded by T. Oiwa, R. Yamada and M. Ohno<sup>18)</sup> from the consideration of chemical reaction that  $\alpha$ - and  $\gamma$ -hepta

have the structure  $I_7$  and  $II_7$  respectively. If this assignment be correct, our computation indicates that  $\gamma$ -hepta should have larger dipole moment than  $\epsilon$ -hepta, which is in accord with the experimental result. The small differences between the observed moments and the calculated ones may be explained as solvent effect similarly as those of monochlorocyclohexane in Table III.

The structures which have the moment close to the observed (2.20 D) of  $\delta$ - and  $\epsilon$ -hepta are  $V_7$  (2.22 D),  $VI_7$  (2.37 D),  $VIII_7$  (1.97 D) and  $IX_7$  (2.20 D). We cannot say, of course, which of these four have the moment assigned to the observed one. But our calculation may be creditable as far as relative values are concerned, which states that  $\delta$ - and  $\epsilon$ -hepta should have the same moment, and the only pair of such structures is  $V_7$  (2.22 D) and  $IX_7$  (2.20 D). This conclusion supports the result of the dehydrogenation and then chlorination of  $\gamma$ -BHC by M. Nakazima and T. Oiwa<sup>7)</sup> and of the chlorination of  $\gamma$ -BHC<sub>2</sub> by T. Oiwa, R. Yamada and M. Ohno<sup>18)</sup>. It may be worth while to mention here that the agreement between the observed moment and the calculated one for these isomers which have a pair of chlorine atoms of short distance confirms our assumption of the induced moment between a pair of C-Cl polar bonds.

5. Assignment of the Configuration of the Isomers of Octa. Both  $\beta$ -p-octa and o-octa have very small moments. The structures having such a small moment are  $I_8$ ,  $III_8$ ,  $XVII_8$  and  $XIII_8$ , of which the last two are too scarce to be taken into account because of larger steric repulsion than the former two forms. According to the fact that  $\beta$ -p-octa is obtained by chlorination of p-dichlorobenzene and o-octa by chlorination of o-dichlorobenzene, the structures of  $\beta$ -p- and o-octa should be assigned to  $III_8$  and  $I_8$  respectively. This assignment agrees with the conclusion from chemical reaction<sup>19)</sup> and are also accepted from the consideration of the relation between melting points, solubility and the symmetry of the molecular forms, just like the isomers of BHC.

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## 綜 説

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### 31. 除虫菊剤の毒作用機構 I. 昆虫毒物学の諸問題 I. 酒井清六

#### 緒 論

除虫菊剤は DDT 及び BHC その他の新有機合成殺虫剤の出現に拘らず、農薬として又防疫用殺虫剤として多大の利用価値を持つている。除虫菊有効成分 Pyrethrins の毒作用機構は Juillet, Everlange et Ancein (42) が昆虫に対して神経筋肉毒として作用し痲痺作用を有すると結論して以来、幾多の学者により病理組織学的、機械電気描寫実験的に、或いは薬劑を局部に処理することに依つて研究されたが今尙不明な點が多い。

特に除虫菊剤の組織化学的な同定が確立されていないので毒作用機構に関する生化学的な知見は皆無に等しい。それ故、化学者に依つて除虫菊の微量分析が確立されることを希望する。

#### (1) 病理組織学的研究

昆虫に対する除虫菊毒作用は主に細胞学的研究より組織学的に研究されている。その障害は表皮、筋肉、神経等に認められ、神経球に於ける空胞、凝集、破壊、Tigrolysis 等の傷害が毒作用の一次的要因と考えられている。しかしこれらの組織変化は除虫菊剤の濃度によつて異つてゐる。

#### 研究方法

Krüger (46) は蚊の 1 種 *Corethra plumicornis* の幼虫及びゴミムシ *Tenebrio molitor* の成虫を除虫菊剤で処理し、その切片の病理組織学的研究をした。その処理昆虫を Alcohol に浸漬し、更に染色し切片を作つてカナダバルサムで封じた。Hartzell & Wilcoxon (30), Wilcoxon & Hartzell (31), Hartzell (24), Klinger (44), Hartzell (25) はゴミムシ *ダマシ*,

マイマイガ *Porthetria dispar* の幼虫、イエバエ *Musca domestica*、セミの 1 種 *Tibicen pruinosa* 及びバツタの 1 種 *Melanoplus femur-rubrum* の夫々の成虫に対して、人体の痲痺の探知の際に用いる Krause (45) の toluidine blue で染色した。Klinger (44) はマイマイガの幼虫の切片を Sudan III; eosin で染色し、Hartzell & Scudder (26) はイエバエの組織障害を鉄 Haematoxylin 及び Erythrsin で染色し、腦の切片は Delafield の Silver albumos (Mallory (49)) や Bodian (2) の Gold chloride 法を用いた。Wigglesworth (79) はサシガメの 1 種 *Rhodonius prolixus* の成虫の切片を Haematoxylin で染色した。Hartzell (25) はイエバエの成虫に対して Haematoxylin と eosin-y との染色法を神経、筋肉に使用した。しかしこの方法は大体適當な方法であつたが Bodian 法の様に良く神経纖維を認め難かつた。Toluidine blue はこの両法より劣る染色法なることを証明した。固定法は古く Krüger (46), Wilcoxon & Hartzell (81), Hartzell (23) 等は一般的な技術を用いた。それらの中の代表的な数例に就いて述べる。

Hartzell (23) は *M. femur-rubrum* の成虫及びゴミムシ *ダマシ* の幼虫の中樞神経系その他の障害を探究するため、6 匹の昆虫を斃死後 Acetone で洗滌し、95% Alcohol 中で解剖した。又对照区の昆虫は除虫菊乳剤の代りに管を切つて殺した。被験昆虫は Wax を底に充した解剖皿に固定し、曲缺を以て氣門線に沿つて切り開いた。更に切開面から消食管を除去し、腹神経索を露出させた。この神経束を齒科用の針で摘出した。腦は頭部を切開し、複眼から視神経に沿つて摘