*The Dipole Moments of the Polyhalocyclohexanes. III**

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In the previous report,1) the configurations of some polyhalocyclohexanes and their related compounds by the dipole moment measurements were discussed, and the dipole moments of polyhalocyclohexanes were calculated by use of our empirical rule and listed in the second article2).

The present work is a report on the result of the investigation of the configurations of some polyhalocyclohexanes; the process is the same as reported earlier1).

Experimental Results

Materials.—The samples were synthesized by one of the present authors (R.R). The dipole moments of these compounds were measured by another (T.S) without further purification.

Dipole Moment Measurement.—The process of the dipole moment measurement is the same as described in our previous article1). The values of the dielectric constant ε and the specific density d measured in different concentrations ω by use of the heterodyne beat apparatus and Ostwald's pycnometer, respectively, are listed in Table A.

The dipole moments were computed by the aid of the equation proposed by Halverstadt-Kumler, and the results are listed in Table B.

Discussion of Results

The five compounds (I to V), which are to be discussed are a kind of chlorine substituted cyclohexanes. Let us discuss their configurations by comparing the observed values of their dipole moments with the calculated ones listed in our previous paper.

In the compound VI, there are two kinds of polar bonds, C–Cl and C–Br, so the observed dipole moment of the compound VI should not be directly referred to the calculated ones. But the difference between the bonds C–Cl (1.86D) and C–Br (1.79D) moments would cause only a small change in the dipole moment of the compound as a whole.

TABLE A

DIELECTRIC CONSTANTS AND SPECIFIC DENSITIES OF BENZENE SOLUTIONS AT 25°C

ω	ε	d	
I. Hexachlorocyclohexane, $C_6H_6Cl_6$			
0.0000	2.2725	0.8719	a=0.25$_9$
0.0091	2.2746	0.8763	b=0.39$_7$
0.0157	2.2753	0.8777	
0.0240	2.2775	0.8818	
0.0503	2.2856	0.8919	
II. 1,1,2,4,4,5-Hexachlorocyclohexane, $C_6H_6Cl_6$			
0.0000	2.2743	0.8716	a=0.22$_8$
0.0353	2.2820	0.8856	b=0.42
0.0689	2.2902	0.9001	
III. Heptachlorocyclohexane, $C_6H_5Cl_7$			
0.0000	2.2730	0.8732	a=0.42
0.0064$_7$	2.2758	0.8761	b=0.49
0.0148$_3$	2.2792	0.8803	
0.0196$_6$	2.2813	0.8829	
IV. Tetrachlorocyclohexane, $C_6H_8Cl_4$			
0.0000	2.2755	0.8745	a=5.02
0.0065$_5$	2.3087	0.8762	b=0.31
0.0109$_2$	2.3303	0.8778	
V. Dodecachlorocyclohexane, C_6Cl_{12}			
0.0000	2.2724	0.8717	a=0.26$_5$
0.0282	2.2808	0.8873	b=0.52$_8$
0.0469	2.2852	0.8966	
0.0602	2.2880	0.9047	
VI. γ-Tetrachlorodibromocyclohexane, $C_6H_6Cl_4Br_2$			
0.0000	2.2724	0.8721	a=2.16
0.0120	2.3012	0.8776	b=0.49$_2$
0.0202	2.3159	0.8824	
0.0524	2.3860	0.8979	

TABLE B

MOLECULAR, ELECTRONIC, AND ATOMIC POLARISATIONS, AND DIPOLE MOMENTS AT 25°C

	Compounds	m.p. (°C)	P(cc.)	P_E+P_A (cc.)	μ D
I.	Hexachlorocyclohexane	109	68.4	59.8	0.65
II.	1,1,2,4,4,5-Hexachlorocyclohexane	156	64.1	59.8	0.46
III.	Heptachlorocyclohexane	119	74.5	64.9	0.69
IV.	Tetrachlorocyclohexane	109	257.9	49.6	3.19
V.	Dodecachlorocyclohexane	285	92.0	90.4	0.28
VI.	γ-Tetrachlorodibromocyclohexane	125	211.4	65.8	2.66

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* The discussion described here was reported on the 7th Annual Meeting of the Chemical Society of Japan. April, 1 (1954).

1) I. Miyagawa, Y. Morino and R. Riemschneider, This Bulletin, 27, 177 (1954).

2) T. Shimozawa, This Bulletin., 28, 389 (1955).

1. Polychlorocyclohexanes

I. Hexachlorocyclohexanes $C_6H_6Cl_6$ (m.p. 109°C).—The observed value of this compound is 0.65D. Considering the accuracy of the dipole moment measurement, the following eleven configurations whose calculated values are less than 1 D, may be selected as the configuration corresponding to this molecule from the Table I in the previous paper;

	Corresponding Nos. in Table I	Configurations	Calculated Moments D
1	1	1e2e3e4e5e6e(β-BHC)	0
2	1′	1a2a3a4a5a6a	0
3	5	1a2e3e4a5e6e(ε-BHC)	0
4	18	1ea2ea4e5e	0.21
5	23	1ea2a3ea5e	0.44
6	25	1ea3ea4a5e	0.22
7	28′	1ea2a3a4ea	0.93
8	30	1ea2e4ea5e	0
9	30′	1ea2a4ea5a	0
10	38	1ea2a3e4e6e	0.49
11	46′	1ea2a3a4e6a	0.21

The observed values of compound I is not completely zero, so the cases 1, 2, 3, 8, and 9 are excluded.

As the starting material of compound I is α−1, 2, 4, 5-tetrachlorocyclohexane, the compound I must have the chlorine atoms at the 1a2a4e5e-positions on the cyclohexane ring, so that the cases 5, 6, 7, 10 and 11 are excluded. Thus, the only configuration compatible with the compound I is the case 4; 1ea2ea4e5e.

The same conclusion is obtained by another argument.

Since the compound I was synthesized by the chlorination of α−1, 2, 4, 5-tetrachlorocyclohexane (1a2a4e5e) (m.p. 174°C),[3] its configuration was considered organochemically to be one of the following three;

a)	1ea2ea4e5e	0.21 D
b)	1ea2ea4a5e	2.15
c)	1ea2a4ea5e	1.88

The calculated moments of these isomers are easily found in Table I in the previous paper; the values are given in the above.

The observed value (0.65D) shows that the configuration (a) corresponds to the compound I, while the other two have definitely too large values to correspond to the compound I.

Thus the configuration of hexachlorocyclohexane (m.p. 109°C) is concluded as 1ea2ea4e5e.

Recently, it was shown that the compound I was synthesized by the chlorination of the 1, 2-dichlorocyclohexadiene (1, 4), too.[4] This fact supports the above statement.

II. Hexachlorocyclohexane $C_6H_6Cl_6$ (m.p. 146°C).—It is sure that the positions of the six atoms of this compound on the cyclohexane ring are 1, 1, 2, 4, 4, and 5.[5]

The configuration of hexachlorocyclohexane, whose chlorine atoms are at the positions 1, 1, 2, 4, 4, 5, are listed below, together with their calculated dipole moment.

	Corresponding Nos. in Table I	Configurations	Calculated Moment	No. of (1a, 3a) pairs
a)	30	1ea2e4ea5e	0 D	0
b)	30′	1ea2a4ea5a	0	2
c)	31	1ea2e4ea5a	1.88	1

The case (c) in the above table is definitely excluded, because its dipole moment is too large compared with the observed one (0.46D). There are two pairs of (1a, 3a) polar bonds in the case (b), but no pairs in the case (a). Since the configuration with (1a, 3a) pairs, (b) is less stable than (a) that without such pairs, the configuration (b) is less plausible. As is well known, the measurement of the dipole moment becomes less accurate as the value approaches 0 D, the difference between the observed (0.46 D) and the calculated values may be ascribed to some error in the measurement.

Thus, the configuration of the hexachlorocyclohexane (m.p. 146°C) is determined as 1ea2e4ea5e.

III. Heptachlorocyclohexane $C_6H_5Cl_7$ (m.p. 119°C).—This compound was synthesized by the chlorination of the both hexachlorocyclohexane (m.p. 109°C, I) and α-1, 2, 4, 5,-tetrachlorocyclohexane (m.p. 174°C).[6]

The dipole moment of this compound was observed to be 0.69D. The configurations whose calculated values of the dipole moment are smaller than 1D are as follows (taken from the Table II in the previous article).

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[3] R. Riemschneider and G. Ottmann, Mitt. II, *Z. Naturforschg.*, 5b, 248 (1950); Mitt. XXXI, 85, 453 (1954). About α-1, 2, 4, 5-Tetrachlorocyclohexane, see Mitt. XII, *Liebigs Ann. Chem.*, 576, 94 (1952).

[4] R. Riemschneider, Mitt. XXXII, *Mh. Chem.*, 86, H, 1/2 (1955) and Mitt. XXXI, *Mh. Chem.*, 85, 453 (1954).

[5] R. Riemschneider, Mitt, I, *Mitt. Physiolog. Chem. Inst. Bln.*, R33, März, 1949; Mitt. IV, V and VI, *Z. Naturforschg.*, 6b, 48, 410, 339 (1951). See also; G. Calingaret, A. J. Kolka, and N. O. Orloff, *J. Am. Chem. Soc.*, 73, 2359 (1951).

[6] l.c. footnote 3).

	Corresponding Nos. in Table II	Configurations	Calculated dipole moment
a)	7	1ea2a3e4e5a6e	0.86 D
b)	14	1ea2ea3a4e5e	0.90
c)	30	1ea2a3e4ea6e	0.87
d)	36	1ea2ea4ea5e	0.85

The synthetic process of this compound suggests that the position of the chlorine atoms were not changed during the reaction. Therefore, six chlorine atoms of the compound III must be at 1ea2ea4e5e, so the cases (a) and (c) are excluded.

However, one can exclude neither of the remaining two (b or d) from the result of the measurement of dipole moment only.

It is suggested, on the other hand in terms of organic chemistry[7], that the hydrogen atom of the group-CHCl is more easily substituted by chlorine than that of $-CH_2$.

The configuration of the compound III, therefore, may be 1ea2ea4ea5e[8].

IV. Tetrachlorocyclohexane $C_6H_8Cl_4$ (m.p. 109°C).—As this compound was obtained by the partial chlorination of cyclohexane, the positions of the chlorine atoms were unknown.

The observed dipole moment was large (3.19 D).

From the Table III in the previous paper, the following five tetrachlorocyclohexanes (upper right) are selected, according to the magnitude of the observed moments (comparable with that of the observed values).

	Corresponding Nos. in Table III	Configurations	Calculated Moment
1	1	1e2e3e4e	3.18 D
2	4	1a2a3e4e	3.03
3	6′	1a2e3e4a	3.18
4	20′	1ea2e4a	3.08
5	29′	1ea2ea	3.36

Another possibility is that the compound IV is a mixture of a pair of inverted isomers. If it were so, the observed value of the dipole moment (3.19 D) would be between the two values calculated for a certain pair of inverted isomers. In this case this compound must have one of the following eight configurations.

Of these, the cases 2 and 8 would be inappropriate. For, in either case one of the inverted isomers is extremely unstable because of the three (1a, 3a) pairs, therefore, the other configuration without such pairs would be predominant, and this stable configuration has, as is seen, definitely smaller dipole moment than that observed for this compound. Nothing more is to be obtained from the result of the measurement of the dipole moment alone. (Table below)

	Stable Forms				Inverted Isomers			
	Correspond Nos. Table III	Configuration	calc.	No. of (1a 3a)	Correspond Nos.	Configuration	calc.	No. of (1a 3a)
1	2	1a2e3e4e	4.14 D	0	2′	1e2a3a4a	2.45 D	1
2	9	1e2a3e5e	2.94	0	9′	1a2e3a5a	4.22	3
3	10	1e2e3e5a	3.65	0	10′	1a2a3a5e	1.52	1
3	11	1a2a3e5e	1.59	0	11′	1e2e3a5a	4.24	1
5	17	1ea2e3e	3.81	0	17′	1ea2a3a	2.54	1
6	18	1ea2a3e	2.76	0	18′	1ea2e3a	4.10	1
7	22	1ea2a5e	2.25	0	22′	1ea2e5a	4.11	1
8	27	1ea3e5e	0.11	0	27′	1ea3a5a	3.72	3

V. Dodecachlorocyclohexane C_6Cl_{12} (m.p. 285°C)[9].—The dipole moment of this molecule is expected to be zero, since this compound has a center of symmetry. The observed dipole moment, 0.28 D, is compatible with this expectation.

2. Polychlorobromocyclohexane

VI. Tetrachlorodibromocyclohexane

$C_6H_6Cl_4Br_2$ (m.p. 123°C)[10].—The positions of halogene atoms of this molecule are, as in the case of BHC, 1, 2, 3, 4, 5, and 6 on the cyclohexane ring. It was hoped that the positions of bromine atoms by the dipole moment investigation could be determined, but it was found to be impossible, since the bond moment of C–Br is comparable to that of C–Cl bond.

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7) l.c. footnote 4).

8) R. Riemschneider, T. Shimozawa and S. Bäker, Mitt. XXXIII, *Z. Naturforschg.*, 9b, 799 (1954).

9) R. Riemschneider and R. Oswald, Mitt. XXXVII, *Mh. Chem.*, 85, 972 (1954).

10) R. Riemschneider and S. Bäker, Mitt. XXIX, *Z. Naturforschg*, 9b, 751 (1954) and *Mh. Chem.*, 85, 1133 (1954). γ-$C_6H_6Cl_4Br_2$, m.p. 123°C shows insecticidal activity, see Table I, p. 1136.

The calculated moments of the hexachlorocyclohexanes with six chlorine atoms at the positions of 1, 2, 3, 4, 5, and 6 are listed below from the Table I in the previous paper (without considering inverted isomer).

1	1e2e3e4e5e6e(β-BHC)	0 D
2	1a2a3e4e5e6e(α-BHC)	2.25
3	1a2a3a4e5e6e(γ-BHC)	2.93
4	1a2e3e4e5e6e(δ-BHC)	2.25
5	1a2e3e4a5e6e(ε-BHC)	0
6	1a2e3a4e5e6e	3.44
7	1a2a3e4a5e6e(η-BHC)	1.88
8	1a2e3a4e5a6e	4.08

It is seen that the case (3) correspounds to the observed value 2.66D, because the difference of the bond moments of C–Cl and C–Br makes the calculated values for the configuration (3) slightly smaller, but it can not be enough to reduce the next higher one, 3.44 D, to the observed value.

Thus, the configuration of the compound VI were determined as the γ-type (aaaeee).

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