The Dipole Moment of the Polyhalocyclohexanes. II. The Calculated Values of Tetrachloro-, Hexachloro-, and Heptachlorocyclohexanes

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The measurement of dipole moment is one of the authentic methods for the determination of the structure of polyhalocyclohexanes[1,2,4]. In order to determine the configuration of molecules by the dipole moment measurement, the observed values of the dipole moment must be compared with the calculated ones. With a view to providing the facility for the determination, the calculated values of the dipole moments of the polyhalocyclohexanes by the aid of Morino-Miyagawa's empirical rule are shown for all kinds of tetrachloro-, hexachloro-, and heptachlorocyclohexanes, in this article.

It is well established that the cyclohexane ring takes the chair form under ordinary condition[4]. The twelve hydrogen atoms, two to each carbon atom, are at the *a*- and *e*-positions, *a*-position being almost parallel to the molecular axis, while *e*-position is in a tetrahedral angle to it and is almost parallel to either of the C–C bonds in the molecule.

In hexachlorocyclohexane, in which the six hydrogen atoms are replaced by chlorine atoms, we have ninety-six isomers by the combination of the positions of the substitution. BHC is a one of the hexachlorocyclohexanes, in which one chlorine atom is attached to each carbon atom. Even in this case, we have eight isomers with respect to the order to the *a*- and *e*-position atoms in the cyclohexane ring. The spatial configuration of the six isomers of BHC already prepared has been determined by the dipole moment measurement[5], by the analysis of crystal structure by X-ray diffraction[6], and by electron diffraction investigation[7]. We have already many isomers of hexachlorocyclohexanes other than BHC. In the course of the determination of their configurations the dipole moment played an important role. Of course some of them were determined from the consideration of the relation to other compounds whose configuration had already been established, but in these cases we found no contradiction of the conclusions obtained from the dipole moments. As already described in the preceding articles[1], the simple rule of vector addition cannot provide enough information for the discussion of the configurations. An empirical rule suggested by Morino and Miyagawa[2,3], which formally took into consideration the moments induced by the bond moments, provided us with reasonable values for many molecules. Indeed, we never found isomers of polyhalocyclohexanes whose observed values were quite different from those computed by our rule.

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

[2] Y. Morino, I. Miyagawa and T. Oiwa; *Botyu-Kagaku*, 15, 181 (1950).

[3] I. Miyagawa; *J. Chem. Soc. Japan*, 75, 1061 (1654).

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

[5] See reference 2) and 3), as examples.

[6] R. G. Dickinson and C. Bilicke; *J. Am. Chem. Soc.*, 50, 764 (1928).

[7] O. Bastiansen, ϕ. Ellefsen and O. Hassel; *Research*, 2, 248 (1949); *Acta Chem. Scand.*, 3, 918 (1949).

Thus it will be useful to calculate the dipole moments from this rule, because reference to these values will enable us to determine the spatial configuration of a given isomer, or at least to confine our calculation to a number of configurations.

The Morino-Miyagawa rule was reported in detail in the preceding articles[2,3]. The calculated values for all kinds of hexachloro-, heptachloro-, and tetrachlorocyclohexanes are listed in Tables I, II, and III,

TABLE I

DIPOLE MOMENT OF HEXACHLOROCYCLOHEXANES

	Configurations (stable form)	D	No. of the (1a, 3a) pairs		Configurations (inverted isomers)	D	No. of the (1a, 3a) pairs
1	1e2e3e4e5e6e(β-BHC)	0	0	1′	1a2a3a4a5a6a	0	6
2	1a2a3e4e5e6e(α-BHC)	2.25	0	2′	1e2e3a4a5a6a	2.26	2
3	1a2a3a4e5e6e(γ-BHC)	2.93	1				
4	1a2e3e4e5e6e(δ-BHC)	2.25	0	4′	1e2a3a4a5a6a	1.71	4
5	1a2e3e4a5e6e(ε-BHC)	0	0	5′	1e2a3a4e5a6a	0	2
6	1a2e3a4e5e6e	3.44	1	6′	1e2a3e4a5a6a	2.59	3
7	1a2a3e4a5e6e(η-BHC)	1.88	1				
8	1a2e3a4e5a6e	4.08	3				
9	1ea2ea3ea	3.71	1				
10	1ea2ea4ea	1.77	1				
11	1ea3ea5ea	1.84	3				
12	1ea2ea3e4e	2.74	0	12′	1ea2ea3a4a	2.81	2
13	1ea2ea3e4a	3.50	1	13′	1ea2ea3a4e	2.42	1
14	1ea2ea3e5e	2.12	0	14′	1ea2ea3a5a	3.66	3
15	1ea2ea3a5e	1.47	1	15′	1ea2ea3a5a	3.31	1
16	1ea2ea3e6e	2.97	0	16′	1ea2ea3a6a	2.98	2
17	1ea2ea3e6a	3.54	1				
18	1ea2ea4e5e	0.21	0	18′	1ea2ea4a5a	2.44	2
19	1ea2ea4e5a	2.15	1				
20	1ea2e3ea4e	3.42	1	20′	1ea2a3ea4a	2.42	2
21	1ea2e3ea4a	3.18	1	21′	1ea2a3ea4e	2.48	1
22	1ea2e3ea5e	1.65	1	22′	1ea2a3ea5a	2.58	3
23	1ea2a3ea5e	0.44	1	23′	1ea2e3ea5a	3.98	3
24	1ea3ea4e5e	2.03	1	24′	1ea3ea4a5a	1.81	3
25	1ea3ea4a5e	0.22	1	25′	1ea3ea4e5a	3.04	3
26	1ea3ea4e6e	2.17	1	26′	1ea3ea4a6a	1.94	2
27	1ea3ea4e6a	1.50	1				
28	1ea2e3e4ea	2.79	0	28′	1ea2a3a4ea	0.93	2
29	1ea2e3a4ea	2.20	1				
30	1ea2e4ea5e(α-1,1,2,4,4,5)	0	0	30′	1ea2a4ea5a	0	2
31	1ea2a4ea5e	1.88	1				
32	1ea2e4ea6e	1.45	0	32′	1ea2a4ea6a	1.80	3
33	1ea2e4ea6a	1.63	1				
34	1ea2e3e4e5e	1.65	0	34′	1ea2a3a4a5a	1.51	4
35	1ea2e3e4e6e	2.16	0	35′	1ea2a3a4a6a	2.10	4
36	1ea2e3e5e6e	1.56	0	36′	1ea2a3a5a6a	2.08	4
37	1ea2a3e4e5e	1.56	0	37′	1ea2e3a4a5a	2.77	3
38	1ea2a3e4e6e	0.49	0	38′	1ea2e3a4a6a	2.70	2
39	1ea2a3e5e6e	1.71	0	39′	1ea2e3a5a6a	3.19	3
40	1ea2a4e5e6e	2.54	0	40′	1ea2e4a5a6a	2.43	2
41	1ea2e3a4e5e	2.30	1	41′	1ea2a3e4a5a	2.16	2
42	1ea2e3a5e6e	3.39	1	42′	1ea2a3e5a6a	1.82	2
43	1ea3a4e5e6e	3.52	1	43′	1ea3e4a5a6a	1.29	2
44	1ea2e3a4e6e	3.54	1	44′	1ea2a3e4a6a	3.16	3
45	1ea2e3e4a5e	1.68	0	45′	1ea2a3a4e5a	1.79	3
46	1ea2e3e4a6e	2.68	0	46′	1ea2a3a4e6a	0.21	2

	Configurations (stable form)	D	No. of the (1a, 3a) pairs		Configurations (inverted isomers)	D	No. of the (1a, 3a) pairs
47	1ea2a3a4e5e	1.27	1	47′	1ea2e3e4a5a	2.87	1
48	1ea2a3a4e6e	1.72	1	48′	1ea2e3e4a5a	3.57	1
49	1ea2a3a5e6e	2.90	1				
50	1ea2a3e4a5e	2.12	1	50′	1ea2e3a4e5a	3.68	3
51	1ea2a3e4a6e	2.41	1	51′	1ea2e3a4e6a	1.81	1
52	1ea2a3e4e5a	1.94	1	52′	1ea2e3a4a5e	1.17	1
53	1ea2a3e5a6e	1.88	1				
54	1ea2a3e4e6a	2.14	1	54′	1ea2e3a4a6e	2.96	1
55	1ea2a3e5e6a	2.15	1	55′	1ea2e3a5a6e	4.50	3

TABLE II

DIPOLE MOMENT OF HEPTACHLOROCYCLOHEXANES

	Configurations (stable form)	D	No. of the (1a, 3a) pairs		Configurations (inverted isomers)	D	No. of the (1a, 3a) pairs
1	1ea2e3e4e5e6e(α-Hepta)	1.04	0	1′	1ea2a3a4a5a6a	1.44	6
2	1ea2a3e4e5e6e(γ-Hepta)	1.26	0	2′	1ea2e3a4a5a6a	2.36	4
3	1ea2e3a4e5e6e	2.66	1	3′	1ea2a3e4a5a6a	1.71	4
4	1ea2e3e4a5e6e(ζ-Hepta)	1.45	0	4′	1ea2a3a4e5a6a	0.68	4
5	1ea2a3a4e5e6e(ε-Hepta)	2.22	1	5′	1ea2e3e4a5a6a	2.48	2
6	1ea2a3e4a5e6e	2.20	1	6′	1ea2e3a4e5a6a	1.73	3
7	1ea2a3e4e5a6e(η-Hepta)	0.86	1	7′	1ea2e3a4a5e6a	1.41	2
8	1ea2a3e4e5e6a	1.97	1	8′	1ea2e3a4a5a6e	2.83	3
9	1ea2e3a4a5e6e(δ-Hepta)	2.20	1	9′	1ea2a3e4e5a6a	1.29	2
10	1ea2e3a4e5a6e	3.44	3	10′	1ea2a3e4a5e6e	2.44	2
11	1ea2ea3e4e5e	1.42	0	11′	1ea2ea3a4a5a	2.35	4
12	1ea2ea3e4e6e	1.57	0	12′	1ea2ea3a4a6a	2.76	4
13	1ea2ea3e5e6a	1.99	1	13′	1ea2ea3a5a6e	3.46	3
14	1ea2ea3a4e5e	0.90	1	14′	1ea2ea3e4a5a	2.70	2
15	1ea2ea4e5a6e	1.97	1	15′	1ea2ea4a5e6a	2.28	3
16	1ea2ea3e5a6e	2.76	1	16′	1ea2ea3a5e6a	1.59	2
17	1ea2ea4a5e6e	2.82	1	17′	1ea2ea4e5a6a	1.14	2
18	1ea2ea3a5e6e	2.56	1	18′	1ea2ea3e5a6a	2.66	2
19	1ea2e3ea5e6e	1.36	1	19′	1ea2a3ea5a6a	1.48	4
20	1ea2e3ea4e6e	2.53	1	20′	1ea2a3ea4a6a	2.39	4
21	1ea3ea4e5e6e	2.06	1	21′	1ea3ea4a5a6a	1.19	4
22	1ea2a3ea4e6e	1.05	1	22′	1ea2e3ea4a6a	3.07	2
23	1ea2a3ea5e6e	1.25	1	23′	1ea2e3ea5a6a	2.83	3
24	1ea2e3ea4e6a	2.48	1	24′	1ea2a3ea4a6e	2.64	2
25	1ea3ea4e5e6a	1.62	1	25′	1ea3ea4a5a6e	1.25	3
26	1ea2e3ea5e6a	1.96	1	26′	1ea2a3ea5a6e	1.91	3
27	1ea2e3ea5a6e	3.47	3	27′	1ea2a3ea5e6a	1.05	2
28	1ea3ea4e5a6e	2.52	3	28′	1ea3ea4a5e6a	0.97	2
29	1ea2e3e4ea6e	1.06	0	29′	1ea2a3a4ea6a	0.82	4
30	1ea2a3e4ea6e	0.87	1	30′	1ea2e3a4ea6a	0.75	2
31	1ea2a4ea5e6e	2.60	1	31′	1ea2e4ea5a6a	1.04	2
32	1ea2e4ea5a6e	1.78	1	32′	1ea2a4ea5e6a	2.23	3
33	1ea2ea3ea4e	3.01	1	33′	1ea2ea3ea4a	3.01	2
34	1ea2ea3ea5e	1.14	1	34′	1ea2ea3ea5a	3.30	3
35	1ea2ea3e4ea	2.74	1	35′	1ea2ea3a4ea	1.99	2
36	1ea2ea4ea5e	0.85	1	36′	1ea2ea4ea5a	1.41	2
37	1ea2ea4ea6e	1.41	1	37′	1ea2ea4ea6a	2.72	3
38	1ea2a3ea5ea	1.00	3	38′	1ea2e3ea5ea	2.09	3

TABLE III

DIPOLE MOMENT OF TETRACHLOROCYCLOHEXANES

	Configurations (stable from)	D	No. of the (1a, 3a) pairs		Configurations (inverted isomers)	D	No. of the (1a, 3a) pairs
1	1e2e3e4e	3.18	0	1′	1a2a3a4a	0.93	2
2	1a2e3e4e	4.14	0	2′	1e2a3a4a	2.45	1
3	1e2a3e4e	2.84	0	3′	1a2e3a4a	2.20	1
4	1a2a3e4e	3.03	0				
5	1a2e3a4e	4.17	1				
6	1e2a3a4e	0.93	0	6′	1a2e3e4a	3.18	0
7	1e2e3e5e	1.96	0	7′	1a2a3a5a	2.50	3
8	1a2e3e5e	1.91	0	8′	1e2a3a5a	2.23	1
9	1e2a3e5e	2.94	0	9′	1a2e3a5a	4.22	3
10	1e2e3e5a	3.65	0	10′	1a2a3a5e	1.52	1
11	1a2a3e5e	1.59	0	11′	1e2e3a5a	4.24	1
12	1e2a3e5a	2.11	0	12′	1a2e3a5e	2.76	1
13	1e2e4e5e(β-1,2,4,5)	0	0	13′	1a2a4a5a	0	2
14	1a2e4e5e	2.65	0	14′	1e2a4a5a	2.27	1
15	1a2a4e5e(α-1,2,4,5)	2.65	0				
16	1a2e4a5e	0	0				
17	1ea2e3e	3.81	0	17′	1ea2a3a	2.54	1
18	1ea2a3e	2.76	0	18′	1ea2e3a	4.10	1
19	1ea2e4e	2.57	0	19′	1ea2a4a	2.79	1
20	1ea2a4e	0.48	0	20′	1ea2e4a	3.08	0
21	1ea2e5e	2.13	0	21′	1ea2a5a	2.36	1
22	1ea2a5e	2.25	0	22′	1ea2e5a	4.11	1
23	1ea2e6e	4.08	0	23′	1ea2a6a	3.30	1
24	1ea2e6a	3.34	0				
25	1ea3e4e	2.21	0	25′	1ea3a4a	1.77	1
26	1ea3e4a	2.24	0	26′	1ea3a4e	2.82	1
27	1ea3e5e	0.11	0	27′	1ea3a5a	3.72	3
28	1ea3e5a	2.15	1				
29	1ea2ea	3.36	0				
30	1ea3ea	2.90	1				
31	1ea4ea	0	0				

where the forms which can be obtained by the inversion of the cyclohexane ring are listed on the same lines. The isomers which are shown in the right half of the tables are the less stable forms with regard to the steric repulsion and designated by primed numbers. The most important part of the steric repulsion of these molecules may be the forces between the chlorine atoms at the 1a-3a positions. The numbers of the pairs of atoms of this sort are listed also in configurations which have reasonable values of dipole moments.

The observed values of dipole moments of the isomers already prepared will be shown in the near future. It will be seen that the agreement between the observed and the calculated values is quite good in all cases, though the assumptions used are of very approximate nature.

It should be noted here that the resultant moment of the molecule arose from the addition of many large C–Cl bond moments (1.86 D). It follows often that the balancing of the large moments yields a small value of the total moment. In this case, the resultant moment largely depends upon the assumed values of induced moments. Actually, the Morino-Miyagawa rule had been proposed to correct the second order quantity. Therefore, we cannot trust the resultant moment, at least when it is smaller than 1.0 D. Of course, when the molecule has a center of symmetry, perfectly cancelling each moment with the corresponding one, a complete vanishing of the total moment results; this phenomenon will be seen, for instances, in the isomers 1,1′,5,30, and 30′ in Table I.

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