halosilanes with the values for the chlorosilanes reveals that the ethyl group is much more positive with respect to silicon than is hydrogen. This is interpreted as a hyperconjugation effect. Replacement of an ethyl by a phenyl group results in an increase in moment for all compounds studied. The alkyl- and phenylsilyl groups are more polarizable than the corresponding hydrocarbon radicals.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Electric Moments of Five of the Isomeric Hexachlorocyclohexanes

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Recent interest in the γ-isomer of hexachlorocyclohexane as an insecticide has given renewed impetus[2] to investigations of the structure of cyclohexane derivatives. The hexachlorocyclohexane molecule affords an unusual opportunity in this connection and, at the same time, structural characterization of its geometric isomers is of considerable interest for the general problem of relating molecular structure and insecticide toxicity. The present investigation is concerned with the determination of the electric moments of the α, β, γ, δ and ϵ isomers of hexachlorocyclohexane. The values obtained resolve some conflicting statements in the literature and provide information which, along with other types of data, help in the elucidation of the structure of the isomers studied.

Experimental

Solvents.—Thiophene-free benzene (Jones and Laughlin reagent grade) which had been stored over sodium was refluxed and distilled over fresh sodium through a 2-meter Dufton column immediately before use. The middle fraction, distilling over a range of 0.02° or less, was collected with precaution to prevent absorption of atmospheric moisture.

1,4-Dioxane (Carbide and Carbon Chemical Corp., C. P. grade) was refluxed over solid potassium hydroxide until a brown precipitate no longer separated on addition of fresh potassium hydroxide. After distillation from the potassium hydroxide, this aldehyde-free dioxane was refluxed with hydrochloric acid as described by Fieser.[3] This was followed by distillation from potassium hydroxide and two distillations from sodium. The second distillation from sodium was a fractionation in a 2-meter Dufton column. The middle fraction with a distilling range of 0.06° or less was collected with precautions to prevent absorption of atmospheric moisture.

Solutes.—The samples of α, β, γ and δ-hexachlorocyclohexane were separated from the crude mixture of isomers using a procedure developed from the method outlined by Slade.[2]

α-Hexachlorocyclohexane was separated from the commercial grades of hexachlorocyclohexane supplied by the Hooker Electrochemical Company. This was recrystallized four times from acetone.[4] The product was recrystallized once from chloroform and 4 times from benzene, m. p. 156.5–157.0°.

The sample of β-isomer was separated from the mixture of isomers prepared by the chlorination of benzene as described by van der Linden.[4] After one recrystallization from methyl acetate, two from 1,4-dioxane and two from benzene a product with a m. p. of 308–309° was obtained. The product showed no detectable pleochroism when examined with a polarizing microscope. The β-isomer is the only reported isomer of hexachlorocyclohexane with a cubic crystal structure.[5] Only a very faint trace of chloride ion was observed in an alcoholic potassium hydroxide solution of the β-isomer after eight hours at 25°. The β-isomer is the only isomer of hexachlorocyclohexane reported to be stable under these conditions.[6]

A sample of γ-isomer[7] was separated from commercial grade hexachlorocyclohexane supplied by the Hooker Electrochemical Company. This was combined with a sample of γ-isomer obtained from E. I. du Pont de Nemours Co. which had been recrystallized from chloroform to the same melting point. The combined sample was recrystallized twice from chloroform, once from carbon tetrachloride and twice from benzene, m. p. 111.5–112.0°.

δ-Hexachlorocyclohexane was separated from the commercial grade mixture of isomers supplied by the Westvaco Chlorine Products Corp., Commercial Solvents Corporation and by E. I. du Pont de Nemours and Co. This was recrystallized twice from carbon tetrachloride and 3 times from benzene, m. p. 136–137°. The sample used for the measurements in benzene was recovered for the measurements in 1,4-dioxane. Disagreement with previous measurements warranted characterization of the sample used in this investigation. Mixed melting points over a range of composition with samples of δ-isomer obtained from the Dow Chemical Co. and the U. S. Department of Agriculture showed no melting point depression. Each of the three δ-isomer samples was found to give the same melting point depression for the same composition of a mixture of α- and δ-isomers. A different but constant melting point depression was observed for the same composition of a mixture of α- and δ-isomers. The refractive indices of the three δ-samples at 145° were found to be approximately 1.513. The solubility of the δ-isomer used in this investigation was determined in ethanol and found to be in reasonable agreement with the high solubility of the δ-isomer reported by Slade.[2] The sample of δ-isomer obtained from the U. S. Department of Agriculture was used to check the measurements in this investigation since the sharp melting point indicated high purity. It was used with no treatment other than drying *in vacuo* over phosphorus pentoxide, m. p. 137.5–138°.

A small amount of ϵ-hexachlorocyclohexane was borrowed from the Dow Chemical Co. and recrystallized twice from benzene, m. p. 216.5–218°. The ϵ-isomer

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[1] Part of the thesis of Edward L. Lind submitted in partial fulfillment of the requirements of the M.A. degree in Chemistry at Duke University, June, 1948.

[2] R. E. Slade, *Chem. and Ind.*, 314 (1945).

[3] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1941, p. 369.

[4] The ratio of α and β solubilities in acetone is unfavorable for the formation of the eutectic of α and β isomers shown to exist by van der Linden, *Ber.*, **45**, 231 (1912).

[5] L. W. Daasch, *Anal. Chem.*, **19**, 779 (1947).

[6] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

[7] Obtained from a methanol solution as described by Slade.[2] A considerable purification was effected by dissolving the crude γ-isomer in chloroform, filtering from the small amount of β-isomer and adding an equal volume of isopropyl alcohol. The purified γ-isomer was found to precipitate from this solution on standing.

TABLE I

Isomer of $C_6H_6Cl_6$	Solvent	Number of solutions	$\Delta E/f_2{}^a$ (av.)	$\Delta d/f_2{}^b$ (av.)	P_2^∞ cc.	$\mu_D{}^c$	
α	C_6H_6	8	6.72 ± 0.02	1.57 ± 0.01	151	2.16	(2.14)
α	1,4-$C_4H_8O_2$	4	8.06 ± 0.15	1.35 ± 0.01	167	2.34	(2.30)
β	C_6H_6	4	0.62 ± 0.02	1.61 ± 0.01	59.2	0.34	0
β	1,4-$C_4H_8O_2$	4	0.81 ± 0.07	1.33 ± 0.01	61.2	0.46	0
γ	C_6H_6	4	11.39 ± 0.04	1.60 ± 0.01	220	2.84	(2.83)
γ	1,4-$C_4H_8O_2$	4	12.93 ± 0.08	1.38 ± 0.01	237	3.00	(2.96)
δ^d	C_6H_6	5	7.23 ± 0.07	1.59 ± 0.01	158	2.24	(2.22)
δ	1,4-$C_4H_8O_2$	4	7.94 ± 0.06	1.36 ± 0.01	165	2.32	(2.28)
ϵ	C_6H_6	4	0.78 ± 0.04	1.64 ± 0.01	60.6	0.43	(0.26)
ϵ	1,4-$C_4H_8O_2$	4	0.86 ± 0.02	1.37 ± 0.01	60.9	0.45	($\sim$0)

[a] The deviations shown here are the average deviations of the mean value, *viz.*, $\frac{\text{av. dev. of a single observation}}{\sqrt{n}}$ where n is the number of independent measurements. [b] The deviations shown here are estimates of the error in the measurement. [c] The values in parentheses in this column are calculated using $P_D = 59.2$ (P_2 for β in C_6H_6) for C_6H_6 as solvent and $P_D = 61.2$ (P_2 for β in 1,4-$C_4H_8O_2$) for 1,4-$C_4H_8O_2$ as solvent. [d] This measurement was checked by a single independent measurement of the dielectric constant of a 0.006 mole fraction solution in C_6H_6 of a sample of δ isomer obtained from the U. S. Department of Agriculture. The $\Delta E/f_2$ for this solution was found to be 6.95. The moment calculated assuming $\Delta d/f_2 = 1.59$ as shown in the above table is 2.13 (2.11)D.

used for the measurements in benzene was recovered for the measurements in 1,4-dioxane.

Apparatus.—The heterodyne heat method of measuring capacity change was used for the measurement of dielectric constant. The oscillator system has been previously described.[8]

The liquid dielectric measuring cell used in this investigation was of the same design as that used by de Bruyne, Davis and Gross.[9] The capacitance change of the cell due to the solvent was measured with a large variable capacitance. The increment in capacitance due to the solute was measured with a small calibrated Wulf (E. Leybold, Nachfolger) precision condenser with a variable capacitance of 30 mmfd. graduated in 5000 scale divisions.

All dielectric constants were measured relative to the dielectric constant of benzene[10] at 30.0°.

The density determinations were made with a conventional pycnometer.[11]

Results

The molar polarization at infinite dilution was calculated from the Hedestrand[12] equation since both density and dielectric constant increments were found to be linear with respect to mole fraction. The form of the equation used was

$$P_2^\infty = \frac{E_1 - 1}{E_1 + 2}\,\frac{1}{d_1}\left(M_2 - \frac{M_1}{d_1}\,\frac{\Delta d}{f_2}\right) + \frac{3M_1}{(E_1 + 2)^2 d_1}\,\frac{\Delta E}{f_2} \qquad (1)$$

where P_2^∞ is the molar polarization of solute at infinite dilution, E the dielectric constant, M the molecular weight, d the density and f the mole fraction. The subscripts 1 and 2 refer to solvent and solute, respectively, while Δd and ΔE are the differences in density and dielectric constant of the solution and the solvent. The values of $\Delta d/f_2$ and $\Delta E/f_2$ used in the above expression were the averages for each series of solutions. All graphs of ΔE against f_2 gave a 0,0 intercept within experimental error.

The electric moment in debye units was calculated from the expression

$$\mu = 0.2231\sqrt{P_2^\infty - R_D} \qquad (2)$$

where the molar refraction, $R_D = 56.9$, was calculated from the refraction equivalents given by Fuchs and Wolf.[13]

The data and results are summarized in Table I. In general the mole fractions of the solutions measured were within the limit 1×10^{-3} and 1.5×10^{-2}. All measurements were made at $30.00 \pm 0.02°$.

Discussion

Table I shows the moments of the β- and ϵ-isomers to be quite small compared to the moments of the α-, γ- and δ-isomers. The small moment observed here for the β-isomer is certainly indistinguishable from zero within experimental error when the uncertainties attributable to solvent effect, and the neglect of atomic polarization, are considered. The β-isomer has been shown to be centrosymmetric,[14] thus one would expect the electric moment to be zero. For purposes of comparison all moments have been calculated using the polarization values of the β-isomer in benzene and 1,4-dioxane as the distortion polarization of the other isomers in the respective solvents. This is seen to have little effect on the moments of the α-, γ- and δ-isomers, but the moment of the ϵ-isomer becomes zero within experimental error.

The electric moment of the β-isomer was first found to be zero in benzene solution by Hassel and Naeshagen[15] and later verified[16] by these authors after Williams and Fogelberg[17] reported the finite value 0.7 D in the same solvent. Williams and

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(8) Weith, Hobbs and Gross, THIS JOURNAL, **70**, 805 (1948).

(9) de Bruyne, Davis and Gross, *ibid.*, **55**, 3936 (1933).

(10) Hartshorn and Oliver, *Proc. Roy. Soc.* (*London*), **A123**, 684 (1929).

(11) Connell, Vosburgh and Butler, *J. Chem. Soc.*, 993 (1933).

(12) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(13) Fuchs and Wolf, "Hand- und Jahrbuch der chemischen Physik," Bd. VI, Abschnitt 1 B, Akad. Verlags., Leipzig, 1935, p. 258.

(14) (a) Hendricks and Bilicke, THIS JOURNAL, **48**, 3007 (1926); (b) Dickinson and Bilicke, *ibid.*, **50**, 764 (1928).

(15) Hassel and Naeshagen, *Tids. Kemi Bergwesen*, **10**, 126 (1930).

(16) Hassel and Naeshagen, *Z. physik. Chem.*, **B15**, 373 (1932).

(17) Williams and Fogelberg, THIS JOURNAL, **53**, 2096 (1931).

Fogelberg also found the anomalous value 2.0 *D* for the β isomer in 1,4-dioxane. The slight increase in the polarization of the β-isomer observed in the present investigation on going from benzene to 1,4-dioxane as solvent is probably attributable to solvent effect. To verify the value of the moment in 1,4-dioxane observed by Williams and Fogelberg a polarization of 140 cc. would have had to be found instead of the 61 cc. actually observed. The electric moment of the ϵ-isomer has not been previously reported.

The electric moment of the α-isomer in benzene reported in Table I is in agreement with the value 2.15 *D* found by Williams and Fogelberg[17] and 2.20 *D* by Hassel and Naeshagen.[15] The moment of this isomer in 1,4-dioxane has not been previously reported.

Only the γ-isomer of these isomers thus far reported in the literature possesses marked insecticidal properties.[2] It is seen that the electric moment of this isomer is the largest of the 5 isomers studied in this investigation; however, it is considerably lower than the value 3.6(5) *D* reported by Melander[18] for a benzene solution at 17°. Our value is in essential agreement with the value 2.89 *D* reported, since the completion of this investigation, by Hetland.[19]

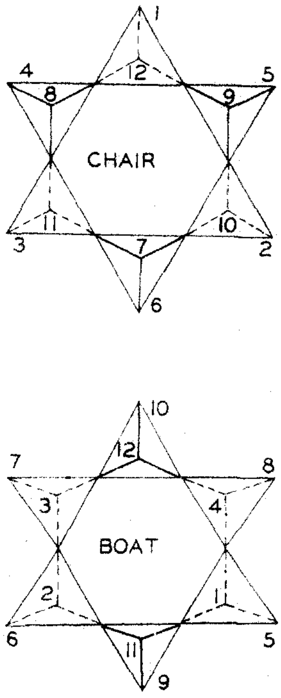

Fig. 1.—The upper figure, 1a, represents the assumed structure of the chair form and the lower figure, 1b, the boat form of the substituted cyclohexane molecule.

The finite moment for the δ-isomer given in Table I is in direct contradiction with the zero moment reported by Melander[18] and it was for this reason that the determination was repeated with a sample from an independent source. The moment, 2.17 *D*, reported by Hetland[19] confirms the presence of a finite dipole moment in this molecule.

van der Linden[4] showed that alkaline dehydrochlorination of the different hexachlorocyclohexanes resulted in different proportions of the isomeric trichlorobenzenes. From this work it was established that the different hexachlorocyclohexanes are geometric isomers and such isomerism has been explained in terms of the boat and chair forms of the cyclohexane ring since these forms involve the least strain.

The thirteen different geometric chair forms and twenty-four different geometric boat forms of the hexachlorocyclohexanes are tabulated in Table II. The six numbers for each form refer to the position of substitution for chlorine atoms as given in Figs. 1a and 1b. An inspection of the Fisher–Hirshfelder models for the chair and boat forms in Table II enabled us to list the various structures in what appears to be the order of increasing strain.

TABLE II

	Chair forms	μ, calcd.	Isomer
1	2, 3, 4, 5, 7, 12	0	ζ, ϵ?
2	2, 3, 5, 6, 8, 12	3.2	α, δ?
3	2, 3, 4, 5, 6, 12	3.2	α, δ?
4	1, 2, 3, 4, 5, 6	0	β
5	3, 4, 5, 6, 10, 12	5.6	
6	1, 2, 4, 7, 9, 11	3.2	α, δ?
7	1, 4, 5, 7, 10, 11	4.6	γ?
8	1, 6, 8, 9, 10, 11	0	ζ, ϵ?
9	1, 4, 7, 9, 10, 11	3.2	α, δ?
10	1, 2, 3, 7, 8, 9	8.0	
11	1, 2, 7, 8, 9, 11	5.6	
12	1, 7, 8, 9, 10, 11	3.2	
13	7, 8, 9, 10, 11, 12	0	
	Boat forms		
14	1, 6, 3, 8, 9, 10	1.8	
15	1, 2, 7, 8, 9, 10	1.8	
16	1, 2, 3, 8, 9, 10	5.0	
17	1, 6, 7, 4, 9, 10	3.8	
18	1, 6, 7, 8, 9, 10	2.0	
19	5, 6, 7, 8, 9, 10	4.0	
20	1, 2, 3, 4, 9, 10	7.6	
21	1, 6, 3, 8, 9, 12	2.6	
22	1, 6, 7, 8, 11, 10	4.2	
23	1, 6, 7, 8, 9, 12	4.4	
24	1, 2, 7, 8, 11, 10	3.2	
25	1, 2, 7, 8, 9, 12	2.8	
26	5, 6, 7, 8, 9, 12	6.4	
27	1, 6, 7, 4, 9, 12	4.2	
28	1, 2, 3, 8, 11, 10	4.2	
29	1, 2, 3, 8, 9, 12	4.2	
30	1, 2, 3, 4, 9, 12	6.2	
31	1, 2, 3, 4, 11, 12	3.8	
32	1, 2, 3, 8, 11, 12	1.9	
33	1, 2, 7, 8, 11, 12	2.0	
34	1, 6, 3, 8, 11, 12	2.0	
35	1, 6, 7, 4, 11, 12	3.8	
36	1, 6, 7, 8, 11, 12	5.2	
37	5, 6, 7, 8, 11, 12	7.8	

The electric moments given in this table were calculated assuming the C–Cl bond moment is 2 *D*, which is the rounded value of the electric moment of monochlorocyclohexane.[16] The calculations were made neglecting any deformation of the normal tetrahedral angle of the carbon atom, Cl–Cl interaction and the influence of the C–H bond moment. In general, taking account of these effects would probably decrease the calculated moments. The last column of Table II lists some tentative assignments of the structures of the sev-

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(18) Melander, *Svensk. Kem. Tids.*, **58**, 231 (1946).

(19) Hetland, *Acta Chem. Scand.*, **2**, 678 (1948).

eral isomers. A discussion of the basis of these assignments follows immediately.

The structure of the β-isomer has been shown by X-ray diffraction studies[14] to be represented by form 4 in Table II. This highly symmetrical structure is in accord with the simple infrared spectrum observed by Daasch,[5] the high melting point of the isomer and the observed very small or zero moment discussed above.

Since the completion of the present work a sixth isomer[20] has been reported and found to have an electric moment of zero.[21] There are thus 3 reported isomers with zero electric moments, *i. e.*, the β-, ϵ- and ζ-isomers. Examination of Table II shows that four, namely, 1, 4, 8 and 13 of the theoretical forms have a calculated zero moment. Hassel and Ottar[22] have described the structure of the β-isomer as an equilibrium between forms 4 and 13 while the structure of the ζ-isomer was considered to be an equilibrium between forms 1 and 8. Since these assignments use all 4 of the theoretical forms with zero moment, the equilibrium theory of Hassel and Ottar does not allow for the existence of more than two isomers with zero moment. This is contradicted by the zero moment found for the ϵ-isomer in this investigation.

If each isomer is to be represented by only one rigid structure and form 4 is assigned to the β-isomer then the structures of the ϵ- and ζ-isomers are to be chosen from the remaining forms with zero moment, *i. e.*, forms 1, 8 and 13. If form 13 is eliminated on the basis of being sterically very improbable, structures 1 and 8 remain as possible choices for the ϵ- and ζ-isomers.

The X-ray analysis of the γ-isomer by Bijvoet[23] has been interpreted as establishing the structure as that given by form 7. The calculated moment of 4.6 *D* and the observed high value of the moment for this isomer lends some support to the choice of this structure.

Slade[2] has chosen form 2 and its mirror image for the structure of the α-isomer, while Melander has chosen form 3. Both structures are consistent with the observed moment and with the general magnitude of the calculated moment.

Both Slade[2] and Melander[18] have chosen form 1 for the structure of the δ-isomer, but the finite moment observed in this investigation and by Hetland[19] is not in accord with the theoretical zero moment for form 1.

The work of Hassel[24] has led to the conclusion that cyclohexane derivatives exist in the chair form. This has been confirmed in part by the chair form structures for the β- and γ-isomers observed in X-ray analysis. If all the hexachlorocyclohexane isomers exist in the chair form, then the structures of the α- and δ-isomers are to be chosen from forms 2, 3, 5, 6, 9, 10, 11 and 12. Of these 2, 3, 6 and 9 are the more probable forms for these isomers when the observed moments and steric factors are considered.

Acknowledgment.—The authors wish to thank the Dow Chemical Company, Midland, Mich., for the use of a sample of the epsilon isomer of hexachlorocyclohexane. They also wish to express their appreciation to the U. S. Department of Agriculture, Hooker Electrochemical Company, E. I. du Pont de Nemours Company, Westvaco Chlorine Products Corp. and Commercial Solvents Corporation for the samples of hexachlorocyclohexane.

Summary

The electric moments of the α-, β-, γ-, δ- and ϵ-isomers of 1,2,3,4,5,6-hexachlorocyclohexane have been determined in two non-polar solvents in order to resolve contradictory and anomalous values in the literature and to provide possible structural information. The results are discussed in relation to possible structure assignments for these isomers.

DURHAM, NORTH CAROLINA RECEIVED APRIL 15, 1950

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[20] NOTE ADDED IN PROOF.—Since the writing of this manuscript. Hassel and co-workers (Bastiansen, Ellefson and Hassel, *Research*, **2**, 248 (1949)) have reported that they are doubtful that the ζ isomer they previously reported[21] is actually an isomer of 1,2,3,4,5,6-hexachlorocyclohexane after having examined the electron diffraction patterns of the whole series of known isomers. A later paper (Bastiansen, Ellefson and Hassel, *Acta Chem. Scand.*, **3**, 918 (1949)) based on the same data makes no mention of the so-called ζ isomer, but reports a zero moment for the ϵ isomer, which is in agreement with the value reported above.

[21] Bastiansen and Hassel, *Acta Chem. Scand.*, **1**, 683 (1947).

[22] Hassel and Ottar, *ibid.*, **1**, 929 (1947).

[23] Bijvoet, *Rec. trav. chim.*, **67**, 777 (1948).

[24] Hassel, *Tids. Kjemi Bergvessen Met.*, **3**, 32 (1943).