[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Dipole Moment Studies of 1,1- and 1,2-Dihalocyclohexanes[1]

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The dipole moments of several 1,1- and *cis*- and *trans*-1,2-dihalocyclohexanes have been determined at 25° in benzene and carbon tetrachloride solutions. The observed moments confirm the structural assignments and provide information concerning configurational equilibria (1a, 2a ⇄ 1e, 2e) of the *trans*-1,2-dihalocyclohexanes.

Introduction

In other work in progress in this Laboratory, pure samples of several 1,2- and 1,1-dihalocyclohexanes were obtained. The dipole moments of these compounds were of interest in connection with structural assignments and are reported in this paper. The use of dipole moments in the study of the molecular structure of such compounds has previously been described by Tulinski, Di Giacomo and Smyth[3] for the isomeric 1,2-dichlorocyclohexanes and by Kozima, Sakashita and Maeda[4] for *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane.

Experimental Details

Materials.—*cis*-[5] and *trans*-1,2-dichlorocyclohexane[6] were prepared and purified by published procedures.[7] *trans*-1,2-Dibromocyclohexane was prepared and purified by the method of Snyder and Brooks.[8] 1,1-Dichlorocyclohexane was prepared by the method of Carroll, *et al.*,[6] and purified by repeated careful fractionations. Eastman Kodak Co. "White Label" grade cyclohexyl chloride was purified by careful fractionation with an efficient glass center-rod column. The preparation and purification of *cis*-1,2-dibromocyclohexane,[9] *cis* and *trans*-1-bromo-2-chlorocyclohexane, 1,1-dibromocyclohexane, and 1-bromo-1-chlorocyclohexane used in the present investigation will be described elsewhere.

Thiophene-free, reagent grade benzene was dried by azeotropic distillation and fractionation. The middle fraction, which was separated for use, had n^{25}D 1.4979. Reagent grade carbon tetrachloride was digested for several days with concentrated sulfuric acid, and, after a preliminary distillation, was fractionated. The middle fraction reserved for use had n^{25}D 1.4573.

Dielectric Constant Measurements.—The heterodyne beat method was adopted for the dielectric constant determinations. The circuit employed was essentially that of Chien[10]; the operating frequency was 500 kilocycles. The precision condenser was calibrated before use as described by Smyth.[11]

The dielectric constant cell was patterned after that described by Albright,[12] except that the outer container was extended vertically to eliminate any danger of contamination of its contents by the thermostat fluid. The unit was constructed of stainless steel with Teflon insulation, held *ca.* 80 ml. of solution, and gave a maximum capacity difference of approximately 100 mmfd. with air as the dielectric. In use, the cell was thermostated in a kerosene bath controlled at 25 ± 0.02°. The lead to the cell was constructed from a section of RG-58 coaxial cable formed into an adequately rigid assembly by use of a copper tubing shield soldered to the coaxial cable fittings. To accommodate the cable, the internal diameter of ordinary 1/4 in. copper tubing was suitably enlarged by etching with nitric acid.

Miscellaneous.—Calibrated weights were used throughout the work reported here, and all results recorded correspond to weights *in vacuo*. Standard pycnometric methods were employed in the required density measurements.

Discussion of Results

A typical set of dielectric constant and density data are presented in Table I and the results of all of the experiments are summarized in Table II. The accuracy of the dielectric constant measurements is estimated at ±0.1%, that of the densities at ±0.03%.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR CIS-1-BROMO-2-CHLOROCYCLOHEXANE AT 25°

n^{25}D 1.5238, d^{25}_4 1.508.

f_2	ϵ	d	f_2	ϵ	d
Benzene solutions			Carbon tetrachloride solutions		
0.00000	2.2737	0.8733	0.00000	2.2275	1.5842
.00841	2.3907	.8811	.00916	2.3414	1.5842
.01530	2.4855	.8877	.01575	2.4247	1.5834
.02301	2.5945	.8948	.01927	2.4714	1.5837
.02988	2.6933	.9012	α =	β =	$P_{2\infty}$ =
α =	β =	$P_{2\infty}$ =	12.73	−0.0363	204 cc.
13.85	0.9131	203 cc.			

TABLE II

SUMMARY OF DIELECTRIC CONSTANT AND DENSITY DATA

Cyclohexane derivative	n^{25}n	d^{25}_4	Solvent	α	β	$P_{2\infty}$ cc.
Chloro	1.4607	0.9940	C_6H_6	6.846	0.200	135
cis-1,2-Dichloro	1.4953	1.199	CCl_4	12.32	−0.4745	200
cis-1,2-Dibromo	1.5518	1.803	C_6H_6	13.74	1.390	199
cis-1,2-Dibromo			CCl_4	12.00	.03609	191
cis-1-Bromo-2-chloro	1.5238	1.508	C_6H_6	13.85	0.9131	203
cis-1-Bromo-2-chloro			CCl_4	12.73	−0.0363	204
trans-1,2-Dibromo	1.5507	1.784	C_6H_6	6.313	1.360	90.6
trans-1,2-Dibromo			CCl_4	4.077	0.3391	61.5
trans-1,2-Dichloro	1.4888	1.180	C_6H_6	9.854	0.4454	146
trans-1-Bromo-2-chloro	1.5173	1.479	C_6H_6	8.663	0.8939	167
1,1-Dichloro	1.4788	1.154	C_6H_6	8.381	0.4180	127
1,1-Dibromo	1.5406	1.746	C_6H_6	8.461	1.352	122

The molar polarization of the solute at infinite

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[2] Du Pont summer research assistant 1954.

[3] A. Tulinski, A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **75**, 3552 (1953).

[4] K. Kozima, K. Sakashita and S. Maeda, *ibid.*, **76**, 1965 (1954).

[5] H. C. Stevens and O. Grummitt, *ibid.*, **74**, 4876 (1952).

[6] B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *ibid.*, **73**, 5382 (1951).

[7] We are indebted to Mr. Herbert Espy for providing us with pure samples of these compounds and to Mr. Leslie Sims for providing samples of the other dihalocyclohexanes used in this work.

[8] H. R. Snyder and L. A. Brooks, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 171.

[9] H. L. Goering, P. I. Abell and B. F. Aycock, Jr., THIS JOURNAL, **74**, 3588 (1952).

[10] J. Y. Chien, *J. Chem. Ed.*, **24**, 494 (1947).

[11] C. P. Smyth, in "Physical Methods of Organic Chemistry," Part II, Chap. XXIV, p. 1005, Interscience Publishers, Inc., New York, N. Y., 1946.

[12] P. S. Albright, THIS JOURNAL, **59**, 2098 (1937).

dilution, $P_{2\infty}$, was calculated by the method of Hedestrand[13] illustrated below

$$P_{2\infty} = A(M_2 - B\beta) + C\alpha$$

$$A = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\frac{1}{d_1};\quad B = \frac{M_1}{d_1};\quad C = \frac{3M_1}{(\epsilon_1 + 2)^2 d_1}$$

$\epsilon_{12} = \epsilon_1 + \alpha f_2$
$d_{12} = d_1 + \beta f_2$
ϵ_1 = dielectric constant of pure solvent
ϵ_{12} = dielectric constant of soln.
d_1 = density of pure solvent
d_{12} = density of soln.
f_2 = mole fraction of solute in soln.
M_1 = mol. wt. of solvent
M_2 = mol. wt. of solute

The values of α and β were obtained in each case by the application of the method of least squares to the appropriate raw data. It is noteworthy that the resulting values for β for benzene solutions agree within 2% with comparison values calculated on the assumption of ideal solution formation. Large differences are observed for carbon tetrachloride solutions.

The dipole moments were calculated from the Debye equation

$$\mu = 0.01281 \times 10^{-18}\,[(P_{2\infty} - R_D)T]^{1/2}$$

The molar refraction of the solute, R_D, was computed from the experimental values of the refractive index and density of the pure liquid. The moments so obtained are tabulated in Table III, the footnote to which gives the several comparison values available.

TABLE III[14]

DIPOLE MOMENTS AND CONFIGURATIONAL EQUILIBRIA OF SOME DIHALOCYCLOHEXANES AT 25°

Solute	$\mu_{obs.} \times 10^{18}$	f_e	f_a	ΔE, ($E_a - E_e$), (cal./mole)
In benzene soln.				
Cyclohexyl chloride	2.24			
cis-1-Bromo-2-chlorocyclohexane	3.15			
cis-1,2-Dibromocyclohexane	3.12			
trans-1,2-Dichlorocyclohexane[a]	2.67	0.75	0.25	650
trans-1-Bromo-2-chlorocyclohexane	2.49	.65	.35	370
trans-1,2-Dibromocyclohexane[b]	2.11	.47	.53	−70
1,1-Dichlorocyclohexane	2.49			
1-Bromo-1-chlorocyclohexane	2.46			
1,1-Dibromocyclohexane	2.44			
In carbon tetrachloride solution				
cis-1,2-Dichlorocyclohexane[c]	3.13			
cis-1-Bromo-2-chlorocyclohexane	3.16			
cis-1,2-Dibromocyclohexane	3.06			
trans-1,2-Dibromocyclohexane[d]	1.74	.32	.68	−400

[a] *Cf.* Smyth's value of 2.66 at 40° and Kozima's value of 2.52 at 30°. [b] *Cf.* Kozima's value of 2.13 at 30°. [c] *Cf.* Kozima's value of 3.1 in preliminary measurements and Smyth's value of 3.13 at 40° in benzene. [d] Identical with Kozima's value of 1.74 at 25°.

It is seen that the measured dipole moments are the same, within experimental error, for all three of the *cis* compounds. It is hence assumed in the following calculations that the C–Cl and C–Br bond moments are indistinguishable for these molecules. The observed moment of 3.13 *D* corresponds to an apparent carbon–halogen bond moment of 1.91 *D*, for the normal tetrahedral carbon bond arrangement, while the dipole moment of cyclohexyl chloride is 2.24 *D*. The difference in these two figures, as pointed out by Smyth,[3] can be attributed to the partial cancellation in the dihalide of the inductive effects of the individual halogen atoms.

trans-1,2-Dihalocyclohexanes exist as equilibrium mixtures of 1e,2e and 1a,2a forms.[3,4,15] The dipole moment of the 1a,2a form, μ_a, may for practical purposes be taken as zero, although it may actually deviate slightly from zero because of inductive effects. If the inductive effects of halogen atoms on adjacent carbon atoms are assumed to be the same for the *cis* and *trans* compounds, the dipole moment μ_e for the *trans*-1e,2e form will be 3.09 *D*, essentially the same as that for the *cis* dihalide. The standard expression for the mean square moment of the mixture

$$\mu^2 = f_e\mu_e^2 + f_a\mu_a^2$$

(f_e, f_a = mole fraction of molecules in 1e,2e, 1a,2a forms) then reduces to

$$\mu^2 = f_e\mu_e^2$$

and the mole fraction of molecules in the 1e,2e configuration can thus be calculated from the observed dipole moment for a *trans* dihalide. The energy difference between the 1a,2a and 1e,2e forms, $\Delta E = E_a - E_e$, can then be calculated from the Boltzmann relation

$$f_a/f_e = (Q_a/Q_e)\,e^{-\Delta E/RT}$$

on the assumption that the ratio of the partition functions of the two forms, (Q_a/Q_e), is unity. The results of such calculations for the *trans* compounds are included in Table II.

An increase in the size of the halogen atoms present in the *trans*-1,2-dihalide should, *ceteris paribus*, increase the energy of the relatively crowded 1e,2e structure compared to that of the 1a,2a structure, with a resultant increase in the equilibrium mole fraction of molecules in the latter form. This effect is considered the primary cause of the trend observed, for benzene solutions, in the configurational equilibria. That bond angle distortion due to halogen size is of secondary importance is shown by the essentially equivalent moments of the three 1,1-dihalides.

The *trans* dibromide has been characterized through electron diffraction studies[15] as an essentially equimolecular mixture of its two stereoisomers. The pronounced solvent effect observed with the *trans* compounds (because of a shift of the configurational equilibria),[2] however, prevents citing the apparent agreement with the present result as significant. The value of 2.67 given here for the dipole moment of *trans*-1,2-dichlorocyclohexane in benzene solution supports the previous value of 2.66 given by Smyth[3] rather than the lower one, 2.53, reported by Kozima, *et al.*[4] That the result of Smyth actually was for 40° rather than 25° does not affect the validity of this comparison since the shift of the configurational equilibrium is negligible for the 15° difference in temperature.

Comparison of the moments of the *cis* com-

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[13] G. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[14] After the manuscript of this paper was submitted, results in excellent agreement with those tabulated here were published by W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. trav. chim.*, **73**, 717 (1954).

[15] O Hassel, *Research*, **3**, 504 (1950); O. Bastiansen and O. Hassel, *Tidsskr. Kjemi Bergv. Met.*, **6**, 96 (1946).

pounds in the two solvents shows, as predicted by Kozima, *et al.*,[2] that there is no apparent solvent effect. The low value for the *cis*-1,2-dibromide is attributed to experimental error, since the pertinent data were in this case the least precise.

It is interesting to note that the observed dipole moment of 2.46 *D* for the 1,1-dihalocyclohexanes corresponds to an apparent carbon–halogen bond moment of 2.17 *D* (assuming a tetrahedral carbon bond arrangement), which is somewhat larger than the corresponding bond moment of 1.9 *D* for the 1,2-dihalides. Evidently the contributions of the cyclohexane carbon–carbon bond moments induced by the halogen atoms (inductive effect) to the apparent carbon-halogen bond moment is larger for 1,1- than for 1,2-dihalocyclohexanes. This is to be expected since the inductive effects of the halogens complement each other in the 1,1-dihalocyclohexanes whereas there is cancellation of inductive effects in the C_1–C_2 bond in the 1,2-dihalides. The contributions of inductive effects to the dipole moment of cyclohexyl chloride (or bromide) should be at least as large as they are to the apparent carbon–halogen moments in 1,1-dihalocyclohexanes. Thus the apparent carbon–halogen moment of 2.17 *D* in 1,1-dihalocyclohexanes would be expected to be a lower limit for the dipole moment of cyclohexyl chloride (or bromide). Because of discrepancies in the values reported for the dipole moment of cyclohexyl chloride,[16,17] 2.07 to 2.30 *D*, and because the lower value, 2.07 *D*, was incompatible with the present results, the dipole moment of this compound was redetermined; a value of 2.24 *D* was obtained.

Iodide ion-promoted dehalogenation and solvolytic reactivities of the 1,2-dihalocyclohexanes here reported will be described in a later paper.

(16) J. W. Williams, THIS JOURNAL, **52**, 1831, 1838 (1930).

(17) O. Hassel and E. Naeshagen, *ibid.*, **19**, 434 (1932).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stereochemistry of Radical Additions. II. The Radical and Ionic Addition of Hydrogen Bromide to 1-Bromocyclohexene and 1-Chlorocyclohexene[1,2]

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Radical additions of hydrogen bromide to 1-bromo- and 1-chlorocyclohexene in pentane give the corresponding *cis*-1,2-dihalocyclohexanes (*trans*-addition) containing less than 1% of the *trans*- isomers. In anhydrous ether radical additions could not be promoted by ultraviolet irradiation and from these reactions only the 1,1-dihalocyclohexanes (products of ionic addition) were isolated. Radical addition is promoted by ultraviolet light in a solvent consisting of 31 mole per cent. ether in pentane and in this solvent the addition appears to be as stereospecific (*trans*-addition) as it is in pentane. The radical addition of hydrogen bromide (initiated by benzoyl peroxide) was also investigated in a homogeneous equimolar mixture of hydrogen chloride and pentane and in this medium the addition is also as stereospecific as it is in pure pentane. Ionic additions of hydrogen bromide to 1-bromo- and 1-chlorocyclohexene give 1,1-dibromocyclohexane and 1-bromo-1-chlorocyclohexane, respectively.

Introduction

In the preceding paper[1] in this series evidence was presented indicating a stereospecific *trans*-addition is involved in the radical addition of hydrogen bromide to 1-methylcyclohexene and 1-bromocyclohexene (Ia). *cis*-1,2-Dibromocyclohexane (IIa), the *trans*-addition product, was the only product isolated from the radical addition of hydrogen bromide to Ia. With 1-methylcyclohexene the radical addition could not be isolated completely from ionic addition and mixtures of 1-bromo-1-methylcyclohexane (the ionic-addition product) and *cis*-1-bromo-2-methylcyclohexane (the *trans*-addition product of radical addition) were obtained. We have extended our studies of the stereochemistry of radical additions and this paper describes radical and ionic additions of hydrogen bromide to 1-bromocyclohexene (Ia) and 1-chlorocyclohexene (Ib) under various conditions.

Radical Additions

The radical addition of hydrogen bromide to 1-chlorocyclohexene (Ib) proceeds rapidly in pentane at 0 and −20° when initiated with ultraviolet light and gives *cis*-1-bromo-2-chlorocyclohexane (IIb) (the *trans*-addition product). It is clear that this is a radical addition since addition does not occur in the absence of irradiation. The observed orientation also indicates that a radical addition is involved. The structure of IIb was established by (1) comparison of its physical properties and infrared spectrum with those of *trans*-1-bromo-2-chlorocyclohexane (IIIb) and 1-bromo-1-chlorocyclohexane (IVb), (2) dehydrobromination (*trans*-elimination),[3] by refluxing with sodium ethoxide in ethanol, to Ib and (3) dipole moment measurements.[4] The *trans*-1-bromo-2-chlorocyclohexane (IIIb) used for comparison was prepared from cyclohexane, N-bromosuccinimide and hydrogen chloride according to a standard procedure for preparing vicinal bromochlorides.[5] This compound, when refluxed with sodium ethoxide in ethanol, was converted to 3-ethoxycyclohexene which was identified by comparison with an authentic sample prepared by the ethanolysis of 3-bromocyclohexene.

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(1) Paper No. 1, H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

(2) This work was supported in part by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

(3) S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

(4) P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955). See also W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. trav. chim.*, **73**, 717 (1954).

(5) J. B. Ziegler and A. C. Shabica, THIS JOURNAL, **74**, 4891 (1952).