

**267.** *Molecular Polarisability: Dipole Moments, Molar Kerr Constants, and Apparent Conformations of Some  $\alpha\omega$ -Dichloro- and -Dibromoalkanes.*

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Dipole moments and molar Kerr constants are calculated for various rotational isomers of ten  $\alpha\omega$ -dihalogenoalkanes, and compared with measurements made on solutions in carbon tetrachloride at 25°. Results are explained by the solutes' being mixtures of isomers. With dichloroethane 73% of *trans*- and 27% of *gauche*-forms appear to be present; with dibromoethane the corresponding figures are 89% and 11%. With the higher members, for which the number of possible conformations is greater, conclusions cannot be definite; specifications are given for those forms in each case which, if present together, could produce  $\mu$ 's and  $mK$ 's consistent with those found.

THIS paper deals with relations between the anisotropies of polarisability and the apparent conformations of "flexible" solute molecules at infinite dilution in non-polar media. In particular it reports an examination of ten molecules of type  $[\text{CH}_2]_n\text{X}_2$  (where  $n = 2, 3, 4, 5$ , or 10, and  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) in carbon tetrachloride at 25°. Observations and results are summarised under usual<sup>1</sup> headings in Tables 1 and 2, after which their interpretations and bearings on previous data are discussed.

#### EXPERIMENTAL

The dihalogenoalkanes were either purified commercial samples or were prepared from the corresponding glycols (cf. Vogel<sup>2</sup>); they were redistilled, and collected at the temperatures

Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405; Le Fèvre and Le Fèvre, *J.*, 1953, 4041; *Rev. Pure Appl. Chem.*, 1955, 5, 261; Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459.

<sup>2</sup> Vogel, "Practical Organic Chemistry," Longmans, London, 3rd edn., 1956, pp. 275—283.

TABLE I.

Incremental Kerr effects, refractive indexes, dielectric constants, and densities of solutions in carbon tetrachloride at 25°.

$10^5 w_2$	$10^7 \Delta B$	$-10^4 \Delta n$	$\epsilon^{25}$	$d_4^{25}$	$10^5 w_2$	$10^7 \Delta B$	$-10^4 \Delta n$	$\epsilon^{25}$	$d_4^{25}$
<i>1,2-Dichloroethane</i>					<i>1,3-Dichloropropane</i>				
1822	0.024	—	2.2999	1.57599	1346	0	—	2.3240	1.57718
3226	0.045	—	2.3586	1.56942	2237	0	—	2.3895	1.57241
3803	0.059	—	2.3829	1.56675	2737	0	—	2.4259	1.56965
4966	0.076	—	2.4345	1.56153	2816	0	5	2.4313	1.56931
7229	0.121	20	2.5377	1.55144	3562	0	6	2.4872	1.56529
8845	0.152	24	2.6157	1.54432	5072	0	8	2.5999	1.55715
whence $10^7 \Delta B = 1.31w_2 + 4.82w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.028$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 4.12w_2 + 2.44w_2^2$ ; $\Sigma \Delta d / \Sigma w_2 = -0.466$ .					whence $\Sigma \Delta n / \Sigma w_2 = -0.017$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 7.27$ ; $\Sigma \Delta d / \Sigma w_2 = -0.542$ .				
<i>1,4-Dichlorobutane</i>					<i>1,5-Dichloropentane</i>				
949	0.019	—	2.2837	1.57863	1183	0.030	—	2.3141	1.57650
1598	0.034	—	2.3240	1.57469	1646	0.044	0	2.3501	1.57331
2055	0.041	—	2.3512	1.57187	2894	0.075	—	2.4453	1.56481
2938	0.058	—	2.4059	1.56651	3473	0.097	—	2.4871	1.56114
3378	0.065	0	2.4370	1.56390	3874	0.110	0	2.5215	1.55822
3565	0.070	1	2.4454	1.56273	5527	0.165	—	2.6441	1.54777
whence $10^7 \Delta B = 2.14w_2 - 5.57w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = -0.002$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 6.09$ ; $\Sigma \Delta d / \Sigma w_2 = -0.616$ .					whence $10^7 \Delta B = 2.40w_2 + 10.8w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = 0$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 7.50$ ; $\Sigma \Delta d / \Sigma w_2 = -0.677$ .				
<i>1,10-Dichlorodecane</i>					<i>1,2-Dibromoethane</i>				
1386	0.035	—	2.3112	1.57124	3621	0.025	1788	—	2.2457
1975	0.053	—	2.3494	1.56566	4701	0.035	1955	—	2.2473
2297	0.064	—	2.3690	1.56237	6058	0.042	3379	—	2.2622
3015	0.085	2	2.4128	1.55646	7528	0.052	4651	25	2.2759
3485	0.098	2	2.4441	1.55108	8397	0.063	5090	—	—
3528	0.103	2	2.4478	1.55079	13,656	0.103	5492	—	2.2855
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 2.76$ ; $\Sigma \Delta n / \Sigma w_2 = -0.006$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 6.19$ ; $\Sigma \Delta d / \Sigma w_2 = -0.960$ .					whence $10^7 \Delta B = 0.679w_2 + 0.556w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = 0.054$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 1.05$ ; $\Sigma \Delta d / \Sigma w_2 = 0.420$ .				
<i>1,3-Dibromopropane</i>					<i>1,4-Dibromobutane</i>				
2749	0	—	2.3393	1.59336	1887	0.026	—	2.2938	1.58874
2998	0	—	2.3477	1.59426	2564	0.037	—	2.3185	1.59026
3410	0	—	2.3654	1.59541	3011	0.044	—	2.3347	1.59120
4878	0	—	2.4268	1.60018	3409	0.049	-19	2.3493	1.59215
6213	0	-35	2.4836	1.60491	4275	0.060	-25	2.3813	1.59416
9241	0	-52	2.6166	—	4883	0.070	-29	2.4043	1.59544
11,612	0	-65	2.7236	1.62281	whence $10^7 \Delta B = 1.44w_2 - 0.100w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = 0.058$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.59$ ; $\Sigma \Delta d / \Sigma w_2 = 0.223$ .				
whence $\Sigma \Delta n / \Sigma w_2 = 0.056$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 3.97$ ; $\Sigma \Delta d / \Sigma w_2 = 0.323$ .					<i>1,10-Dibromodecane</i>				
<i>1,5-Dibromopentane</i>					<i>1,10-Dibromodecane</i>				
1243	0.029	—	2.2834	1.58609	1082	0.034	—	2.2757	1.58159
1682	0.039	—	2.3035	1.58670	1119	0.037	—	2.2775	1.58176
1951	0.043	—	2.3162	1.58700	1325	0.042	—	2.2873	1.58124
3401	0.078	-20	2.3840	1.58890	1711	0.054	-8	2.3040	1.58015
4473	0.106	-27	2.4349	1.59029	2042	0.068	-10	2.3188	1.57919
whence $10^7 \Delta B = 2.19w_2 + 3.95w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = 0.059$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 4.59$ ; $\Sigma \Delta d / \Sigma w_2 = 0.127$ .					whence $10^7 \Delta B = 3.03w_2 + 12.8w_2^2$ ; $\Sigma \Delta n / \Sigma w_2 = 0.048$ ; $\Sigma \Delta \epsilon / \Sigma w_2 = 4.51$ ; $\Sigma \Delta d / \Sigma w_2 = -0.258$ .				

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations on solutions in carbon tetrachloride at 25°).

Solute	$\alpha\epsilon_1$	$\beta$	$\gamma$	$\delta$	$\infty P_2$ (c.c.)	$R_D$ (c.c.)	$\mu$ (D) *	$\infty({}_mK_2) \times 10^{13}$
Cl·[CH <sub>2</sub> ] <sub>2</sub> ·Cl ...	4.12	-0.294	-0.019	18.7	66.7	21.1	1.47	13.4
Cl·[CH <sub>2</sub> ] <sub>3</sub> ·Cl ...	7.27	-0.342	-0.012	0	114.8	25.5	2.07	-1.7 <sub>6</sub>
Cl·[CH <sub>2</sub> ] <sub>4</sub> ·Cl ...	6.09	-0.389	-0.001	30.6	114.3	30.4	2.01	27.7
Cl·[CH <sub>2</sub> ] <sub>5</sub> ·Cl ...	7.50	-0.427	0	34.3	149.0	34.6	2.35	34.0
Cl·[CH <sub>2</sub> ] <sub>10</sub> ·Cl ...	6.19	-0.606	-0.004	39.4	200.7	58.8	2.61	50.3
Br·[CH <sub>2</sub> ] <sub>2</sub> ·Br ...	1.05	0.265	0.037	9.70	46.2	27.1	0.93	13.9
Br·[CH <sub>2</sub> ] <sub>3</sub> ·Br ...	3.97	0.204	0.038	0	114.4	31.4	1.99	-1.7 <sub>0</sub>
Br·[CH <sub>2</sub> ] <sub>4</sub> ·Br ...	3.59	0.141	0.040	20.6	116.1	36.0	1.96	31.8
Br·[CH <sub>2</sub> ] <sub>5</sub> ·Br ...	4.59	0.080	0.041	31.3	150.6	40.7	2.30	51.7
Br·[CH <sub>2</sub> ] <sub>10</sub> ·Br	4.51	-0.163	0.033	43.3	207.3	64.4	2.61	95.0

\* It is assumed that  ${}_D P = 1.05R_D$ .

shown, immediately before the solutions were made up: 1,2-dichloroethane, b. p. 84°; 1,3-dichloropropane, b. p. 120—122°; 1,4-dichlorobutane, b. p. 160°; 1,5-dichloropentane, b. p. 84°/22 mm.; 1,10-dichlorodecane, b. p. 130—132°/6—7 mm.; 1,2-dibromoethane, b. p. 131°; 1,3-dibromopropane, b. p. 165—166°; 1,4-dibromobutane, b. p. 88°/16—18 mm.; 1,5-dibromopentane, b. p. 114—116°/20 mm.; 1,10-dibromodecane, m. p. 27°.

Details of procedures, apparatus, computational methods, symbols used, etc., are given in refs. 1. For pure carbon tetrachloride (*i.e.*, when  $w_2 = 0$  in Table 1) at 25°, the properties indicated have values as follows:  $\epsilon$  (dielectric constant) = 2.2270;  $d$  (density) = 1.58454;  $n$  (refractive index) = 1.4575;  $B$  (Kerr constant) =  $0.070 \times 10^{-7}$ .

*Previous Measurements.*—Dipole-moment determinations made before 1948 are listed by Wesson<sup>3</sup> in Tables which contain no values for 1,4-dichlorobutane, 1,5-dichloropentane, and 1,10-dichlorodecane. Since 1948 the following solution measurements ( $D$ ) have been published by Ketelaar and van Meurs:<sup>4</sup> 1,2-dibromoethane 0.94—0.95, 1,3-dibromopropane 1.98—2.00, 1,4-dibromobutane 1.92—1.95, 1,5-dibromopentane 2.24—2.27, and 1,10-dibromodecane 2.51—2.57. Only determinations made in carbon tetrachloride at 20°, as calculated from the Debye equation, are given above; however, this reference<sup>4</sup> lists also measurements at different temperatures in benzene, dioxan, n-hexane, cyclohexane, and in the pure liquid state. Gas measurements are recorded after 1948 as: 1,2-dichloroethane<sup>5</sup> 1.91—1.84 at 302—337° K, 1,4-dichlorobutane<sup>6</sup> 2.22 at 160—235°.

$K$  ( $= B\lambda/n$ ) for gaseous 1,2-dichloroethane at 108.5° has been reported<sup>7</sup> as  $4.7 \times 10^{-15}$ , for light of wavelength 546 m $\mu$  and a pressure of 760 mm. Molar Kerr constants of 1,2-dichloroethane and 1,2-dibromoethane (in carbon tetrachloride) have been given as  $(15.7—16.0) \times 10^{-12}$  and  $(17.5—17.8) \times 10^{-12}$ , respectively, by Marinin<sup>8</sup>—these were stated to be almost independent of temperature (15—70°).

## DISCUSSION

*Molar Kerr Constants in Relation to Conformations.*—Our approach is to calculate the  ${}_mK$ 's and the moments expected for various possible conformations and to compare the results with the corresponding observed quantities.

For each particular model considered a symmetric matrix

$$\begin{bmatrix} b_{xx} & b_{yx} & b_{zx} \\ b_{xy} & b_{yy} & b_{zy} \\ b_{xz} & b_{yz} & b_{zz} \end{bmatrix}$$

defines the molecular polarisability tensor referred to an arbitrarily selected system of cartesian co-ordinate axes  $X, Y, Z$ . The matrix is not in general diagonal: the principal

<sup>3</sup> Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

<sup>4</sup> Ketelaar and van Meurs, *Rec. Trav. chim.*, 1957, **76**, 437.

<sup>5</sup> Jatkar and Phansalkar, *J. Univ. Poona Sci. Techn.*, 1954, 59.

<sup>6</sup> Oriani and Smyth, *J. Chem. Phys.*, 1949, **17**, 1174.

<sup>7</sup> Stuart and Volkmann, *Ann. Phys.*, 1933, **18**, 121.

<sup>8</sup> Marinin, *Zhur. Fiz. Khim.*, 1953, **27**, 988.

axes transformation which makes it so is effected on the Sydney University digital computer Silliac, an eigenvalue-eigenvector programme being available in the computing library. Tables 3—7 list the principal polarisabilities and their locations with respect to  $X, Y, Z$  for the structures shown.

Certain details of bond polarisabilities and of molecular geometry are required for these calculations. The anisotropic polarisabilities of C-Cl and C-Br are taken as in methyl chloride and methyl bromide (Le Fèvre and Le Fèvre, 1955, p. 300), *viz.*:  $b_L^{C-Cl} = 0.318$ ,  $b_T^{C-Cl} = b_V^{C-Cl} = 0.220$ ,  $b_L^{C-Br} = 0.465$ ,  $b_T^{C-Br} = b_V^{C-Br} = 0.308$  (all as units  $10^{-23}$  c.c.). For the C-C bond, polarisability semi-axes (*viz.*,  $b_L^{C-C} = 0.098_6$ ,  $b_T^{C-C} = b_V^{C-C} = 0.027_4$ ) extracted from cyclohexane<sup>9</sup> are used; and for the isotropically polarisable<sup>1</sup> C-H bond,  $b_L^{C-H} = b_T^{C-H} = b_V^{C-H} = 0.064 \times 10^{-23}$  c.c. The C-C-Cl, C-C-Br, and C-C-C bond angles are assumed to be  $110^\circ$  throughout: small deviations from this angle do not sensitively affect the calculations. Bond moments for C-Cl and C-Br are adopted as 1.86 and 1.82 D, respectively. The nomenclature followed for the various forms is that described in ref. 10, p. 560.

1,2-Dichloro- and 1,2-Dibromo-ethane.—Ainsworth and Karle<sup>11</sup> showed that for 1,2-dichloroethane, the *gauche*-forms are generated by rotating  $\text{CH}_2\text{Cl}$   $109^\circ \pm 5^\circ$  from the *trans*-structure; this has been accepted as such in the present work, but for  $\text{X}[\text{CH}_2]_n\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) where  $n > 2$ , the *gauche*-positions are regarded as requiring  $120^\circ$  rotations from the *trans*. Computed values of the molecular polarisability semi-axes, their locations with respect to the orthogonal axes  $X, Y, Z$ , resultant dipole moments, and molar Kerr constants for the *trans*-, *gauche*-, and *cis*-rotational isomers are summarised in Table 3.

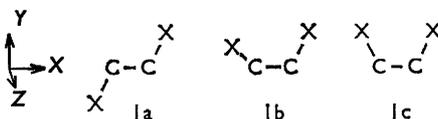


TABLE 3.

## 1,2-Dichloroethane

Direction cosines with

Formula	Calc. $b \times 10^{23}$	$X$	$Y$	$Z$	$\mu_{\text{res}}$ (calc.)	$mK \times 10^{12}$ (calc.)
1a <i>trans</i>	$b_1 = 0.783$	+0.875	-0.484	0	0	1.6 <sub>4</sub>
	$b_2 = 0.931$	+0.484	+0.875	0		
	$b_3 = 0.723$	0	0	+1		
1b <i>gauche</i>	$b_1 = 0.759$	+0.530	-0.492	+0.691	2.8 <sub>5</sub>	35
	$b_2 = 0.840$	+0.848	+0.301	-0.436		
	$b_3 = 0.838$	+0.006	+0.817	+0.577		
1c <i>cis</i>	$b_1 = 0.818$	+1	0	0	3.5 <sub>0</sub>	172
	$b_2 = 0.897$	0	+1	0		
	$b_3 = 0.723$	0	0	+1		
1,2-Dibromoethane						
1a <i>trans</i>	$b_1 = 0.960$	+0.906	-0.423	0	0	4.3
	$b_2 = 1.224$	+0.423	+0.906	0		
	$b_3 = 0.899$	0	0	+1		
1b <i>gauche</i>	$b_1 = 0.941$	+0.662	-0.435	+0.610	2.7 <sub>8</sub>	72
	$b_2 = 1.083$	-0.001	+0.814	+0.581		
	$b_3 = 1.059$	-0.749	-0.385	+0.539		
1c <i>cis</i>	$b_1 = 1.007$	+1	0	0	3.4 <sub>2</sub>	292
	$b_2 = 1.177$	0	+1	0		
	$b_3 = 0.899$	0	0	+1		

Leybold models indicate that the *cis*-forms are sterically improbable. Reed and Lipscomb<sup>12</sup> have stated that at  $-140^\circ$  the molecule of 1,2-dichloroethane exists in the

<sup>9</sup> Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

<sup>10</sup> Brown and Sheppard, *Proc. Roy. Soc.*, 1955, *A*, 231, 563.

<sup>11</sup> Ainsworth and Karle, *J. Chem. Phys.*, 1952, 20, 425.

<sup>12</sup> Reed and Lipscomb, *Acta Cryst.*, 1953, 6, 45.

*trans*-configuration; electron-diffraction data led Ainsworth and Karle<sup>11</sup> to believe that at 22° the amount of *gauche*-isomer is  $27 \pm 5\%$ . For a mixture of the *trans*- (73%) with the *gauche*-isomer (27%) of 1,2-dichloroethane, the following are predicted:

$$\mu \text{ (calc.)} = 1.4_8 \text{ D; } {}_mK \text{ (calc.)} = 10.6_5 \times 10^{-12},$$

in reasonable accord with the observed values of 1.47 D and  $13.4 \times 10^{-12}$ , respectively.

For 1,2-dibromoethane a mixture of the *trans*- (89%) with the *gauche*-isomer (11%) yields:

$$\mu \text{ (calc.)} = 0.93 \text{ D; } {}_mK \text{ (calc.)} = 11.7_5 \times 10^{-12},$$

again in reasonable accord with the observed values of 0.93 D and  $13.9 \times 10^{-12}$ , respectively.

*1,3-Dichloro- and 1,3-Dibromo-propane.*—Four rotational isomers can be predicted for each of these molecules (Formulae 2a—d), but examination of molecular models shows that the *gauche-gauche*'-isomers must be extremely unstable because of steric interference between the halogen atoms. Computed values for the other three configurations are given in Table 4.

The observed values, from Table 2, are:

$$\begin{array}{c} \text{1,3-Dichloropropane} \\ \mu_{\text{obs}} = 2.07 \text{ D; } \infty({}_mK_2) = -1.8 \times 10^{-12}. \end{array}$$

$$\begin{array}{c} \text{1,3-Dibromopropane} \\ \mu_{\text{obs}} = 1.99 \text{ D; } \infty({}_mK_2) = -1.7 \times 10^{-12}. \end{array}$$

Clearly none of the three isomers 2a—c can be favoured or, alternatively, eliminated on such evidence. This is not incompatible with the spectroscopic studies by Brown and Sheppard,<sup>10</sup> and it appears that contributions from all three are present in solution at ordinary temperatures. A marked simplification of the infrared spectra was observed on crystallisation and, from assignments of C—X stretching frequencies for *trans*- and *gauche*-dispositions and from symmetry considerations, Brown and Sheppard concluded that the solid-state isomer is the non-planar *gauche-gauche*-conformation.

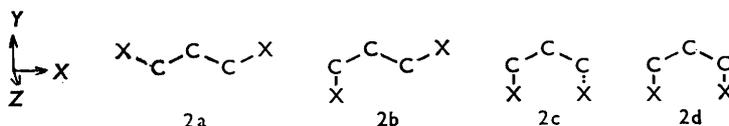


TABLE 4.

		1,3-Dichloropropane				
		Direction cosines with				
Formula	Calc. $b \times 10^{23}$	X	Y	Z	$\mu_{\text{res}}$ (calc.)	${}_mK \times 10^{12}$ (calc.)
2a <i>trans-trans</i>	$b_1 = 1.106$	+1	0	0	2.1 <sub>3</sub>	0.6
	$b_2 = 0.990$	0	+1	0		
	$b_3 = 0.879$	0	0	+1		
2b <i>trans-gauche</i>	$b_1 = 1.073$	+0.800	+0.565	-0.203	2.1 <sub>5</sub>	1.6
	$b_2 = 0.992$	-0.565	+0.594	-0.573		
	$b_3 = 0.910$	-0.203	+0.573	+0.794		
2c <i>gauche-gauche</i>	$b_1 = 0.974$	+1	0	0	2.1 <sub>6</sub>	0.1
	$b_2 = 0.992$	0	+1	0		
	$b_3 = 1.009$	0	0	+1		
		1,3-Dibromopropane				
2a <i>trans-trans</i>	$b_1 = 1.361$	+1	0	0	2.0 <sub>9</sub>	1.9
	$b_2 = 1.205$	0	+1	0		
	$b_3 = 1.055$	0	0	+1		
2b <i>trans-gauche</i>	$b_1 = 1.322$	+0.712	+0.640	-0.291	2.1 <sub>0</sub>	2.4
	$b_2 = 1.207$	-0.640	+0.420	-0.643		
	$b_3 = 1.091$	-0.289	+0.644	+0.709		
2c <i>gauche-gauche</i>	$b_1 = 1.150$	+1	0	0	2.1 <sub>1</sub>	0.8 <sub>5</sub>
	$b_2 = 1.207_5$	0	+1	0		
	$b_3 = 1.263$	0	0	+1		

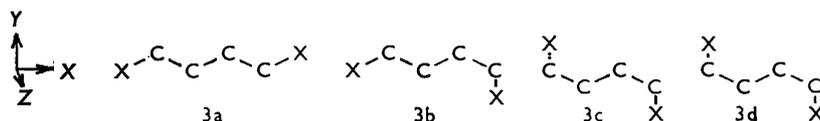


TABLE 5.

Formula	Calc. $b \times 10^{23}$	Direction cosines with			$\mu_{\text{res}}$ (calc.)	$mK \times 10^{12}$ (calc.)
		X	Y	Z		
1,4-Dichlorobutane						
3a <i>trans-trans</i>	$b_1 = 1.331$	+0.940	+0.342	0	0	3.2
	$b_2 = 1.148$	-0.342	+0.940	0		
	$b_3 = 1.034$	0	0	+1		
3b <i>trans-gauche'</i>	$b_1 = 1.246$	+0.978	+0.200	-0.063	3.0 <sub>4</sub>	65
	$b_2 = 1.190$	-0.207	+0.872	-0.443		
	$b_3 = 1.076$	-0.034	+0.446	+0.894		
3c <i>gauche-gauche'</i>	$b_1 = 1.267$	+0.268	-0.715	+0.646	0	1.4
	$b_2 = 1.176$	+0.939	+0.044	-0.342		
	$b_3 = 1.069_5$	+0.216	+0.698	+0.683		
3d <i>gauche'-gauche'</i>	$b_1 = 1.208$	+0.743	-0.669	0	3.0 <sub>3</sub>	-10
	$b_2 = 1.140$	+0.669	+0.743	0		
	$b_3 = 1.164$	0	0	+1		
1,4-Dibromobutane						
3a <i>trans-trans</i>	$b_1 = 1.620$	+0.900	+0.436	0	0	6.4
	$b_2 = 1.329$	-0.436	+0.900	0		
	$b_3 = 1.210$	0	0	+1		
3b <i>trans-gauche'</i>	$b_1 = 1.484$	+0.832	+0.508	-0.223	2.9 <sub>7</sub>	120
	$b_2 = 1.410$	-0.543	+0.663	-0.515		
	$b_3 = 1.265$	-0.114	+0.550	+0.828		
3c <i>gauche-gauche'</i>	$b_1 = 1.247$	+0.231	+0.735	+0.637	0	3.5
	$b_2 = 1.357$	-0.966	+0.098	+0.238		
	$b_3 = 1.554$	+0.112	-0.671	+0.733		
3d <i>gauche'-gauche'</i>	$b_1 = 1.333$	+0.848	+0.530	0	2.9 <sub>6</sub>	47
	$b_2 = 1.407$	-0.530	+0.848	0		
	$b_3 = 1.418$	0	0	+1		

1,4-Dichloro- and 1,4-Dibromo-butane.—The four conformations examined are represented by Fig. 3a—d; throughout it is assumed that the carbon skeleton remains planar. The calculations are summarised in Table 5. Observed values are:

$$\mu_{\text{obs}} = 2.01 \text{ D}; \quad \infty(mK_2) = 27.7 \times 10^{-12}.$$

$$\mu_{\text{obs}} = 1.96 \text{ D}; \quad \infty(mK_2) = 31.8 \times 10^{-12}.$$

These suggest that mixtures of polar and non-polar isomers occur together in almost equal proportions, and that within the ~50% polar constituent, conformation 3b outweighs 3d in 1,4-dichlorobutane, but that the reverse is the case for the dibromo-analogue.

1,5-Dichloro- and 1,5-Dibromo-pentane.—Table 6 summarises the physical constants calculated for four conformations. The observed values are:

$$\mu_{\text{obs}} = 2.35 \text{ D}; \quad \infty(mK_2) = 34.0 \times 10^{-12}.$$

$$\mu_{\text{obs}} = 2.30 \text{ D}; \quad \infty(mK_2) = 51.7 \times 10^{-12}.$$

These cannot be accounted for by a mixture of *trans-trans*-, *trans-gauche*-, and *gauche-gauche*-forms alone; this indicates that, unlike the 1,3-dihalogenopropanes, there is participation in the mixture of isomers of the now sterically allowable *gauche-gauche'*-form.

1,10-Dichloro- and 1,10-Dibromo-decane.—Computed values for the four conformations considered (analogous to Fig. 3a—d) are summarised in Table 7. Observed values are:

$$\mu_{\text{obs}} = 2.61 \text{ D}; \quad \infty(mK_2) = 50.3 \times 10^{-12}.$$

$$\mu_{\text{obs}} = 2.61 \text{ D}; \quad \infty(mK_2) = 95.0 \times 10^{-12}.$$

TABLE 6.  
1,5-Dichloropentane  
Direction cosines with

Conformn.	Calc. $b \times 10^{23}$	X	Y	Z	$\mu_{\text{res}}$ (calc.)	$mK \times 10^{12}$ (calc.)
<i>trans-trans</i>	$b_1 = 1.512$	+1	0	0	2.1 <sub>3</sub>	2.2
	$b_2 = 1.348$	0	+1	0		
	$b_3 = 1.190$	0	0	+1		
<i>trans-gauche</i>	$b_1 = 1.466$	+0.916	+0.392	-0.086	2.1 <sub>5</sub>	2.9
	$b_2 = 1.349$	-0.392	+0.827	-0.404		
	$b_3 = 1.234$	-0.088	+0.403	+0.911		
<i>gauche-gauche</i>	$b_1 = 1.381$	+1	0	0	2.1 <sub>6</sub>	0.9
	$b_2 = 1.349$	0	+1	0		
	$b_3 = 1.320$	0	0	+1		
<i>gauche-gauche'</i>	$b_1 = 1.381$	+1	0	0	3.7 <sub>2</sub>	155
	$b_2 = 1.428$	0	+0.761	-0.649		
	$b_3 = 1.241$	0	+0.649	+0.761		
1,5-Dibromopentane						
<i>trans-trans</i>	$b_1 = 1.768$	+1	0	0	2.0 <sub>9</sub>	3.9
	$b_2 = 1.563$	0	+1	0		
	$b_3 = 1.366$	0	0	+1		
<i>trans-gauche</i>	$b_1 = 1.707$	+0.841	+0.516	-0.161	2.1 <sub>0</sub>	3.8
	$b_2 = 1.565$	-0.516	+0.677	-0.525		
	$b_3 = 1.423$	-0.162	+0.525	+0.836		
<i>gauche-gauche</i>	$b_1 = 1.557$	+1	0	0	2.1 <sub>1</sub>	0.3
	$b_2 = 1.565$	0	+1	0		
	$b_3 = 1.574$	0	0	+1		
<i>gauche-gauche'</i>	$b_1 = 1.557$	+1	0	0	3.6 <sub>4</sub>	323
	$b_2 = 1.421$	0	+0.717	+0.697		
	$b_3 = 1.718$	0	-0.697	+0.717		

If the assumption is valid that the carbon chain is coplanar, then the mixture of isomers appears to contain a 3 : 1 mixture of polar : non-polar constituents; in both cases the *trans-gauche*-conformation seems to predominate.

TABLE 7.  
1,10-Dichlorodecane  
Direction cosines with

Conformn.	Calc. $b \times 10^{23}$	X	Y	Z	$\mu_{\text{res}}$ (calc.)	$mK \times 10^{12}$ (calc.)
<i>trans-trans</i>	$b_1 = 2.540$	+0.981	+0.193	0	0	11.8
	$b_2 = 2.231$	-0.193	+0.981	0		
	$b_3 = 1.967$	0	0	+1		
<i>trans-gauche'</i>	$b_1 = 2.463$	+0.998	+0.058	-0.006	3.0 <sub>4</sub>	70
	$b_2 = 2.252$	-0.058	+0.977	-0.205		
	$b_3 = 2.022$	-0.006	+0.205	+0.979		
<i>gauche-gauche'</i>	$b_1 = 2.405$	+0.967	-0.242	+0.073	0	4.6
	$b_2 = 2.281$	+0.250	+0.865	-0.435		
	$b_3 = 2.051$	+0.043	+0.439	+0.897		
<i>gauche'-gauche'</i>	$b_1 = 2.404$	+0.979	-0.205	0	3.0 <sub>3</sub>	-223
	$b_2 = 2.237$	+0.205	+0.979	0		
	$b_3 = 2.097$	0	0	+1		
1,10-Dibromodecane						
<i>trans-trans</i>	$b_1 = 2.820$	+0.954	+0.300	0	0	16.6
	$b_2 = 2.421$	-0.300	+0.954	0		
	$b_3 = 2.143$	0	0	+1		
<i>trans-gauche'</i>	$b_1 = 2.686$	+0.982	+0.184	-0.031	2.9 <sub>7</sub>	126
	$b_2 = 2.474$	-0.185	+0.934	-0.304		
	$b_3 = 2.223$	-0.027	+0.305	+0.952		
<i>gauche-gauche'</i>	$b_1 = 2.596_5$	+0.771	-0.545	+0.329	0	5.1
	$b_2 = 2.541$	+0.634	+0.609	-0.476		
	$b_3 = 2.246$	+0.059	+0.576	+0.815		
<i>gauche'-gauche'</i>	$b_1 = 2.582$	+0.965	-0.264	0	2.9 <sub>6</sub>	-158
	$b_2 = 2.450$	+0.264	+0.965	0		
	$b_3 = 2.351$	0	0	+1		

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[Received, August 24th, 1961.]