ELECTRIC MOMENT AND MOLECULAR STRUCTURE. VIII. COMPLEX DIPOLES AND LONG-CHAIN MOLECULES

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Previous papers have treated the moments of the ethyl esters of dicarboxylic acids,[1] the glycols,[2] and the polymethylene bromides[3] and the results obtained in these papers have been graphically examined by Ebert and Höjendahl,[4] whose conclusions are in essential agreement with those drawn in the original papers. It has seemed desirable to measure tetramethylene bromide for comparison with the bromides containing three-carbon and five-carbon chains and to measure in benzene solution the other long-chain bromides which were previously measured in heptane, thus obtaining data under identical conditions for careful comparison. Other more or less similar molecules have been studied and the data will be subjected to a quantitative treatment in an attempt to gain further information concerning the resolution of two or more moments in a molecule and the shape of a long carbon chain.

Resolution of Moments

In the ethylene halide molecules, rotation around the C–C bond makes it possible for the dipoles to occupy different positions relative to one another, the positions not being equally probable, however, because of the mutual potential energies of the dipoles and of steric effects. This problem has been treated in a previous paper.[5] Since, in more complex molecules, it becomes even more difficult to calculate the potential energy and its effect upon the oscillation of the dipoles, we shall, in these calculations, disregard the mutual potential energies of the dipoles, their variable inductive effects upon one another, and steric effects, and assume that, in rotation about any single bond, all positions are equally probable. Cases in which the results of these calculations may be thrown into serious error by the neglected potential energy may then be examined qualitatively. With the assistance of Dr. Henry Eyring, each type of molecule was treated separately in order to derive an equation for its moment, but, finally, the matrix algebra was employed by Dr. Eyring[6] to derive a general equation, from which the equations for the different types could be derived. The equations for the moments of the particular molecules studied here are

[1] Smyth and Walls, THIS JOURNAL, 53, 527 (1931).

[2] Smyth and Walls, ibid., 53, 2115 (1931).

[3] Smyth and Kamerling, ibid., 53, 2988 (1931).

[4] Ebert and Höjendahl, Z. physik. Chem., [B] 15, 74 (1931).

[5] Smyth, Dornte and Wilson, THIS JOURNAL, 53, 4242 (1931).

[6] Eyring, Phys. Rev., 38, 746 (1932).

given below, the bond moments being represented by m, the carbon valence angle by θ, taken as $110°$,[7] and the oxygen valence angle by α, also taken as $110°$ in the calculations for Table IV

$$Br(CH_2)_nBr \quad m_1 = C\text{—}Br, \mu = m_1 \sqrt{2 - 2(-\cos\theta)^n}$$

$$CH_2BrCHBrCH_2Br \quad m_1 = C\text{—}Br, \mu = m_1 \sqrt{3 + 4\cos^2\theta + 2\cos^3\theta}$$

$$HO(CH_2)_2OH \quad m_2 = C\text{—}O, m_3 = H\text{—}O,$$

$$\mu = \sqrt{2(m_2^2 + m_3^2 - m_2^2\cos^2\theta - m_3^2\cos^2\alpha\cos^2\theta + 2m_2m_3\cos\alpha\sin^2\theta)}$$

$$Cl(CH_2)_2OH \quad m_1 = C\text{—}Cl, m_2 = C\text{—}O, m_3 = H\text{—}O,$$

$$\mu = \sqrt{m_1^2 + m_2^2 + m_3^2 - 2m_1m_2\cos^2\theta + 2m_2m_3\cos\alpha - 2m_1m_3\cos\alpha\cos^2\theta}$$

$$Cl(CH_2)_3OH, \text{ or } Br(CH_2)_3OH \quad m_1 = C\text{—}Cl \text{ or } C\text{—}Br, m_2 = C\text{—}O, m_3 = H\text{—}O,$$

$$\mu = \sqrt{m_1^2 + m_2^2 + m_3^2 + 2m_1m_2\cos^3\theta + 2m_2m_3\cos\alpha + 2m_1m_3\cos\alpha\cos^3\theta}$$

$(CH_2XCH_2)_2O \quad m_1 = C\text{—}X, m_3 = $ resultant of two C—O moments, which acts in the line bisecting α, $\mu = \sqrt{2m_1^2 + m_3^2 + 2m_1^2\cos^5\theta - 4m_1m_3\cos^2\theta\cos\theta}/2$

Preparation of Materials

Heptane, benzene,[8] trimethylene bromide[3] and dioxane,[2] were purified as in earlier work. The dioxane was kept standing over sodium and was freshly distilled just before using. Its physical constants depended somewhat upon the duration of the drying and were newly determined for each lot used.

Tetramethylene Bromide.—Furfuran obtained from the Miner Laboratories, Chicago, was converted into tetrahydrofuran under the direction of Dr. Wallace H. Carothers of E. I. du Pont de Nemours and Company by catalytic reduction in butyl alcohol solution. This material, having been purified by fractional distillation, was treated with three times the theoretical amount of 48% hydrobromic acid. After heating at 100–105° for seven to eight hours, the reaction mixture was very slowly distilled and the heavy layer of tetramethylene bromide in the distillate was separated, the yield being 70% of the theoretical. Experiments carried out at a slightly higher temperature with a more rapid distillation of the product led to decomposition and a decreased yield. As suggested by Dr. J. R. Johnson in a communication to Dr. Carothers, a little pure ethyl bromide was added as a solvent to prevent the formation of troublesome emulsions, and the mixed bromides were washed with ice water, with cold strong sulfuric acid, with water, twice with dilute sodium bicarbonate solution, and several times with water. The product was dried with anhydrous calcium chloride, the ethyl bromide distilled off with a steam-bath and the residual tetramethylene bromide fractionally distilled under reduced pressure. The fraction distilling at 85–85.5° (18 mm.) was redistilled; b. p. 81° (15 mm.).

Pentamethylene Bromide.—Material kindly loaned by Dr. Carothers was dried with anhydrous calcium chloride and fractionally distilled under reduced pressure; b. p. 106.9–107.4° (24 mm.).

Decamethylene Bromide.—Material loaned by Dr. Carothers was distilled under reduced pressure; b. p. 182–183° (22 mm.). The material was further purified by three fractional crystallizations; m. p. 23.5°.

1,2,3-Tribromopropane.—Material obtained from the Eastman Kodak Company (b. p. 143–145°, 80 mm.) was dried with anhydrous calcium chloride and fractionally distilled under reduced pressure; b. p. 96.0–96.2° (13 mm.).

[7] Smyth and Walls, THIS JOURNAL, **54**, 1854 (1932).

[8] Ref. 7, p. 1857.

Ethylene Chlorohydrin.—Material from the Dow Chemical Company was twice fractionally distilled; b. p. 128.1–128.2° (752 mm.).

Trimethylene Chlorohydrin.—Material from the Eastman Kodak Company was twice fractionally distilled under reduced pressure; b. p. 66.0–66.2° (16 mm.).

Trimethylene Bromohydrin.—Material from the Eastman Kodak Company was fractionally distilled under reduced pressure three times; b. p. 77–78° (16 mm.).

β,β′-Dichloroethyl Ether.—Material loaned by Dr. W. L. Ruigh of Merck and Co., Inc. (a fraction of some material obtained from the Carbide and Chemical Company) was dried with anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 75.0 ±0.1° (20 mm.).

β,β′-Diiodoethyl Ether.—Material loaned by Dr. Ruigh, which had become slightly colored from standing, was twice shaken with "Darco" to remove coloration, then shaken with mercury, dried over anhydrous calcium chloride and twice fractionally distilled under reduced pressure; b. p. 102.3 ±0.1° at 4 mm., distilling at the rate of four drops in three seconds with the bath at 130°.

The densities and refractive indices given in Table II may be taken as criteria of purity.

Experimental Results

The densities and dielectric constants of the solutions of the polar substances in the non-polar were measured with the apparatus and methods previously employed,[1] a wave length of 1000 meters being used in the dielectric constant determinations. In Table I the first column gives the mole fraction c_2 of the polar substance in the solution and the succeeding columns give the values at 25 and 50° of the dielectric constants ϵ, the densities d of the solutions and the polarizations P_2 of the polar substance. The values of the moment in Table III were obtained as in previous papers.[1]

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

c_2	ϵ 25°	50°	d 25°	50°	P_2 25°	50°
		Benzene–Trimethylene Bromide				
0.00000	2.276	2.226	0.8734	0.8465	(26.68	26.76 = P_1)
.01145	2.340	2.284	.8881	.8610	109.7	105.4
.01591	2.367	2.305	.8938	.8665	110.9	104.1
.01826	2.380	2.317	.8965	.8689	111.0	105.6
.03719	2.490	2.414	.9203	.8924	110.6	105.0
.04701	2.548	2.464	.9324	.9042	110.5	104.6
.07254	2.696	2.597	.9639	.9352	108.5	103.6
.11556	2.948	2.824	1.0166	.9869	105.3	101.4
		Benzene–Tetramethylene Bromide				
0.01344	2.354	2.297	0.8905	0.8631	117.5	114.6
.02002	2.392	2.332	.8986	.8711	117.6	114.7
.02546	2.424	2.360	.9055	.8780	117.4	114.0
.04549	2.542	2.465	.9301	.9022	116.8	112.7
.09057	2.813	2.712	.9846	.9558	114.6	111.2
.11226	2.944	2.828	1.0104	.9812	113.3	109.9

TABLE I (*Continued*)

c_2	ϵ 25°	50°	d 25°	50°	P_2 25°	50°
			Heptane–Tetramethylene Bromide			
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.03680	2.035	1.992	.7137	.6913	114.5	113.4
.05889	2.107	2.058	.7346	.7117	113.7	111.9
.07512	2.163	2.110	.7496	.7265	114.2	112.2
.11276	2.296	2.233	.7859	.7618	113.2	111.4
			Benzene–Pentamethylene Bromide			
0.00862	2.337	2.280	0.8843	0.8573	140.4	133.5
.01416	2.376	2.315	.8913	.8641	140.4	134.1
.02387	2.447	2.377	.9033	.8758	141.5	134.9
.03153	2.504	2.431	.9126	.8851	141.8	136.9
.04047	2.571	2.491	.9234	.8959	141.8	136.5
.04621	2.612	2.528	.9304	.9026	141.0	135.9
.07320	2.814	2.709	.9634	.9352	138.7	133.9
.10953	3.071	2.941	1.0039	.9755	134.8	130.6
			Benzene–Decamethylene Bromide			
0.01580	2.417	2.353	0.8920	0.8650	194.4	187.6
.02617	2.510	2.434	.9036	.8766	194.4	186.5
.03814	2.615	2.528	.9166	.8896	193.2	185.7
.05744	2.776	2.673	.9365	.9095	189.8	183.1
.07771	2.939	2.821	.9564	.9294	186.8	180.8
			Benzene–1,2,3-Tribromopropane			
0.01262	2.325	2.270	0.8988	0.8713	89.3	87.0
.02432	2.369	2.312	.9219	.8940	89.2	87.6
.04719	2.457	2.391	.9666	.9380	89.2	86.7
.07055	2.547	2.472	1.0123	.9827	88.5	85.9
.08908	2.618	2.538	1.0474	1.0174	88.2	85.8
			Heptane–1,2,3-Tribromopropane			
0.03737	1.996	1.954	0.7311	0.7082	84.4	82.5
.06351	2.053	2.006	.7680	.7441	84.5	82.6
.11246	2.165	2.108	.8375	.8124	84.8	82.4
.15218	2.265	2.197	.8956	.8693	85.1	82.3
			Benzene–Ethylene Chlorohydrin			
0.01247	2.338	2.280	0.8764	0.8492	90.8	86.1
.01776	2.366	2.306	.8776	.8505	92.0	88.1
.03051	2.438	2.367	.8806	.8533	94.5	89.0
.03193	2.445	2.371	.8808	.8536	94.3	89.1
.04086	2.494	2.417	.8830	.8559	93.7	88.7
.06225	2.628	2.534	.8881	.8607	95.6	90.7
.08002	2.740	2.628	.8924	.8651	95.5	90.0
.08288	2.761	2.647	.8933	.8659	95.7	90.4
.18405	3.584	3.343	.9193	.8916	96.4	91.1

<div align="center">TABLE I   (Concluded)</div>

c_2	ϵ 25°	50°	d 25°	50°	P_2 25°	50°

1,4-Dioxane (n_D^{20} 1.42310)–Ethylene Chlorohydrin

c_2	25°	50°	25°	50°	25°	50°
0.00000	2.261	2.214	1.0312	1.0027	(25.27	25.30 = P_1)
.01946	2.388	2.329	1.0363	1.0079	106.0	101.4
.03465	2.488	2.418	1.0382	1.0098	105.2	100.6
.05234	2.614	2.531	1.0405	1.0120	105.5	101.2
.05963	2.665	2.579	1.0414	1.0130	105.1	101.1
.08114	2.824	2.718	1.0441	1.0157	104.2	99.9

<div align="center">Benzene–Trimethylene Chlorohydrin</div>

0.02042	2.414	2.351	0.8781	0.8511	120.7	116.9
.03818	2.538	2.464	.8825	.8555	120.2	116.6
.05889	2.688	2.601	.8872	.8602	118.2	115.1
.08343	2.877	2.769	.8932	.8663	117.1	113.7
.11879	3.161	3.025	.9016	.8748	114.9	111.7
.14638	3.407	3.238	.9086	.8817	113.7	110.3

<div align="center">1,4-Dioxane (n_D^{20} 1.42320; n_D^{25} 1.42085)–Trimethylene Chlorohydrin</div>

0.00000	2.217	2.176	1.0311	1.0026	(24.65	24.74 = P_1)
.02758	2.422	2.363	1.0303	1.0016	129.5	125.5
.04378	2.551	2.478	1.0316	1.0032	128.4	123.6
.07720	2.831	2.724	1.0346	1.0064	125.5	120.3
.08517	2.894	2.783	1.0353	1.0073	124.1	119.3
.12558	3.247	3.094	1.0387	1.0110	120.1	115.5

<div align="center">Benzene–Trimethylene Bromohydrin</div>

0.01631	2.385	2.326	0.8847	0.8578	121.1	117.5
.02979	2.479	2.410	.8938	.8666	121.7	117.7
.06778	2.756	2.656	.9204	.8928	119.5	115.0
.07527	2.812	2.708	.9255	.8980	118.9	114.7
.08427	2.882	2.769	.9319	.9042	118.4	114.1

<div align="center">Benzene–β,β'-Dichloroethyl Ether</div>

0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.01595	2.425	2.354	.8805	.8535	168.4	157.1
.02437	2.507	2.424	.8842	.8572	168.3	156.4
.03968	2.656	2.555	.8909	.8639	166.1	155.7
.05689	2.836	2.703	.8984	.8714	165.2	153.8
.08033	3.083	2.913	.9086	.8815	162.4	151.7
.09818	3.283	3.077	.9161	.8890	160.8	150.1
.12253	3.555	3.307	.9263	.8991	157.7	147.8

<div align="center">Benzene–β,β'-Diiodoethyl Ether</div>

0.00000	2.2755	2.2255	0.8733	0.8464	(26.66	26.74 = P_1)
.01287	2.372	2.311	.9030	.8753	148.7	141.7
.02350	2.451	2.381	.9266	.8986	148.0	140.7
.03131	2.509	2.432	.9441	.9159	146.8	139.4
.04295	2.595	2.507	.9694	.9407	145.4	138.2
.04999	2.648	2.555	.9850	.9556	144.5	138.1
.05509	2.683	2.587	.9956	.9662	143.6	137.4

TABLE II

REFRACTIVE INDICES AND DENSITIES OF THE PURE LIQUIDS

	d_4^{25}	d_4^{50}	n_D^{20}	n_D^{25}
Trimethylene bromide	1.9701	1.9250	1.52319	1.52090
Tetramethylene bromide	1.8177	1.7786	1.51908	1.51685
Pentamethylene bromide	1.6927	1.6574	1.51255	1.51028
Decamethylene bromide	1.349	1.3223	.....	1.4914
1,2,3-Tribromopropane	2.4076	2.3586	1.58594	1.58349
Ethylene chlorohydrin	1.1947	1.1671	1.44208	1.44012
Trimethylene chlorohydrin	1.1260	1.1022	1.44586	1.44418
β,β'-Dichloroethyl ether	1.2139	1.1844	1.45750	1.45534
β,β'-Diiodoethyl ether	2.3317	2.2855	.....	.....

TABLE III

REFRACTIONS, ORIENTATION POLARIZATIONS AND ELECTRIC MOMENTS

Compound	Solvent	MR_D	$P_\infty - MR_D$ 25°	50°	$\mu \times 10^{18}$ 25°	50°
Trimethylene bromide	Benzene	31.20	81.1	75.4	1.97	1.98
Tetramethylene bromide	Benzene	35.93	83.0	79.3	2.00	2.03
Tetramethylene bromide	Heptane		79.8	77.9	1.96	2.01
Pentamethylene bromide	Benzene	40.64	105.1	99.7	2.25	2.28
Decamethylene bromide	Benzene	63.9[a]	134.3	125.7	2.54	2.56
1,2,3-Tribromopropane	Benzene	39.01	51.1	48.7	1.57	1.59
1,2,3-Tribromopropane	Heptane		45.3	43.6	1.48	1.51
Ethylene chlorohydrin	Benzene	17.76	73.7	68.7	1.88	1.89
Ethylene chlorohydrin	1,4-Dioxane		88.7	83.9	2.07	2.09
Trimethylene chlorohydrin	Benzene	22.31	100.2	96.2	2.19	2.24
Trimethylene chlorohydrin	1,4-Dioxane		110.4	105.7	2.30	2.35
Trimethylene bromohydrin	Benzene	25.2[a]	98.1	93.8	2.17	2.21
β,β'-Dichloroethyl ether	Benzene	31.98	138.5	127.0	2.58	2.57
β,β'-Diiodoethyl ether	Benzene	47.39[a]	103.7	95.6	2.23	2.23

[a] Calculated from measurements upon solutions.

Discussion of Results

The values for the moments of trimethylene bromide, pentamethylene bromide and decamethylene bromide are 0.2×10^{-18} lower than the corresponding values previously found in heptane solution.[3] As the value given in Table III for tetramethylene bromide in benzene is higher than that in heptane by an amount too small to be significant and as the values for the ethylene halides are decidedly higher in benzene than in heptane, the reason for the discrepancy is not apparent. The bromides used were the same materials employed in the previous measurements, and had been subjected to further purification without appreciable alteration of the refractive indices. As the present measurements form part of a long series carried out with great care in the same way, they will be regarded as correct. In any event, the small difference does not materially affect the conclusions to be drawn.

The value for ethylene chlorohydrin is 0.20×10^{-18} higher in dioxane

than in benzene solution, while the trimethylene compound is 0.11×10^{-18} higher. As dioxane may introduce complications through compound formation with the solute, it appears probable that the values obtained in benzene are the more accurate, the possible error in the dioxane values decreasing with increasing separation of the dipoles. This suggests that the values obtained for the two- and three-carbon glycols in dioxane solution[2] may be from 0.1–0.3×10^{-18} high, which would make the moments of ethylene and propylene glycol about 2.0×10^{-18}. The values for the six- and ten-carbon glycols should be but little low, as the two hydroxyl groups should be almost independent of one another at these distances and it was shown that butyl alcohol had almost the same moment in dioxane as in benzene solution. However, it appears consistent to lower the former values for the three-, six- and ten-carbon glycols by 0.2×10^{-18}.

In the quantitative treatment of these moments, the results of which are given in Table IV, a value of 1.5×10^{-18} is assigned to the C–Br moments in 1,2,3-tribromopropane, as in ethylene bromide, 1.7×10^{-18} to the C–Br moments in trimethylene bromide, and 1.9×10^{-18} in the three longer molecules.[3] The difference in the values used is the result of a rough approximation made in an attempt to take care of the small effects of induction upon the carbon chain and of the possible C–H moments. The lumping of these effects in a single moment in the C–Br line may introduce an error of as much as 0.2×10^{-18}, but in the four-, five- and ten-carbon molecules, at least, the error should be practically the same. The other moments used in Table IV are taken from data previously summarized.[9] The possible error resulting from the assumption that the

TABLE IV
CALCULATED AND OBSERVED VALUES OF MOMENTS ($\times 10^{18}$)

	m_1	m_2	m_3	μ calcd.	μ obs.
$Br(CH_2)_2Br$	1.5			1.99	0.8–1.05
$Br(CH_2)_3Br$	1.7			2.36	1.98
$Br(CH_2)_4Br$	1.9			2.67	2.01
$Br(CH_2)_5Br$	1.9			2.68	2.28
$Br(CH_2)_{10}Br$	1.9			2.69	2.56
$CH_2BrCHBrCH_2Br$	1.5			2.36	1.58
CH_2OHCH_2OH		0.7	1.6	2.1	2.0
$CH_3CHOHCH_2OH$		.7	1.6	2.1	2.0
$HO(CH_2)_3OH$		.7	1.6	2.1	2.3
$HO(CH_2)_6OH$		.7	1.6	2.1	2.3
$HO(CH_2)_{10}OH$		.7	1.6	2.1	2.3
CH_2ClCH_2OH	1.9	7	1 6	2.41	1.89
$CH_2ClCH_2CH_2OH$	1.9	.7	1.6	2.42	2.24
$CH_2BrCH_2CH_2OH$	1.9	.7	1.6	2.42	2.21
$(CH_2ClCH_2)_2O$	1.9		1.14	2.94	2.57
$(CH_2ICH_2)_2O$	1.6		1.14	2.43	2.23

[9] Eucken and Meyer, *Physik. Z.*, **30**, 387 (1929); Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, Inc., New York, 1931.

oxygen valence angle is 110° is no greater than that in the values for the C–O and H–O moments.

The moment of the ethylene bromide molecule is far lower than the calculated value because the two C–Br dipoles lower each other's moments by greater inductive action as they approach more closely the *cis* position, the position of maximum resultant moment, because the mutual potential energy of the dipoles tends to make this *cis* position least probable,[5] and because of the interatomic forces characterized by the term "steric effect." This steric effect is so complicated by the necessity of considering the interaction of bromine with bromine, bromine with hydrogen, and hydrogen with hydrogen, that the quantitative treatment of all the combined effects requires a separate communication. As is to be expected, these effects diminish with increasing length of the carbon chain until, in decamethylene bromide, the difference between the observed and the calculated values is less than the probable error, and the increase of the moment with rising temperature has disappeared. Calculation shows that if pentamethylene bromide had an extended rod-like molecule, the potential energy between the two C–Br dipoles would still not be wholly negligible in comparison with kT, as it is in an extended decamethylene bromide molecule. If there is sufficient freedom of rotation about the C–C bonds to give a great variety of forms to the molecules, those forms in which the dipoles point more or less in the same direction should be less probable in the shorter molecules and the moments should be smaller than the calculated values, the difference decreasing with increasing length of the chain. The observed and calculated values of decamethylene bromide are indistinguishable from that which would result from a completely random orientation of the two dipoles relative to each other. This theory of more or less free rotation about the C–C bonds explains all the results for the polymethylene bromides except the close proximity of the value for tetramethylene bromide to that of trimethylene bromide.

From preliminary considerations it appears that a hydrocarbon chain is in a position of minimum potential energy when in the zigzag form indicated for it in solids, in films, and even in liquids.[10] For the polymethylene bromides, this would give structures somewhat as follows:
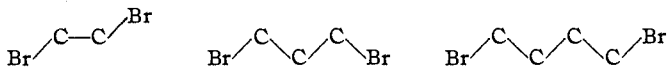
etc. The C-Br dipoles would not necessarily cancel each other in the even-numbered chains as shown above, but there would certainly be a sharp alternation of moment in going up the series. If there is freedom of rotation only about the end C–C bonds, where the inhibition of rotation should be less than in the case of a bond with another C–C on each side, it is evident

[10] Gane and Ingold, *J. Chem. Soc.*, 2153 (1931); Ingold, *ibid.*, 2170 (1931).

that the even-numbered molecules should have moments equal to the value 2.52×10^{-18} calculated for the ethylene compound and the odd-numbered molecules values equal to that for the trimethylene compound, 2.63×10^{-18}, the C–Br moment being taken as 1.9×10^{-18}. The differences between these values and those calculated for the longer molecules on the assumption of free rotation about the C–C bond are not sufficient to permit of distinction between the fixed and the variable structures. However, the fact that a higher moment is indicated for the odd-numbered molecules offers an explanation of the proximity of the moment of tetramethylene bromide to that of trimethylene bromide, while, if there were freedom of rotation about the C–C bonds, it should be closer to the value for pentamethylene bromide. The moment calculated for 1,2,3-tribromopropane is much higher than the observed values in Table IV because of these same effects.

The reason that the observed moments of ethylene and propylene glycol do not lie far below the calculated as in the case of ethylene bromide is apparent when the structure is considered. If, as an extreme case, the potential energy between the dipoles caused the hydroxyls to occupy a *trans* position, $\overset{\text{HO}}{\diagdown}\text{C}{-}\text{C}\overset{}{\underset{\text{OH}}{\diagdown}}$, a position in which ethylene bromide would have zero moment, the two C–O moments would cancel each other, but the two H–O moments would rotate around the extensions of the C–O lines in such a way that their mutual potential energies would lower the resultant moment only a little below the calculated value in Table IV. Evidently, little lowering of the moment below the calculated value is to be expected unless there is a tendency toward ring formation in the longer molecules and the uniformity of the observed values indicates the absence of such formation. It is not surprising, therefore, to find in the longer glycols the only case in Table IV in which the observed moments are higher than the calculated, the difference very possibly arising from the use of too low values for the C–O moment, if not for the H–O. If the not unreasonable value 1.1×10^{-18} is used for the C–O moment, the calculated value for the glycols is 2.25×10^{-18}. As is to be expected, the behavior of the chloro- and bromohydrins is intermediate between that of the glycols and that of the polymethylene halides. The trimethylene compounds have moments not far below the calculated and the same is true of the β,β'-dihalogenated ethers.

It has not seemed worth while to calculate the moments of the diethyl esters of the dicarboxylic acids because each half of the molecule contains three dipoles, one C=O and two C–O, the moments of which, as well as the angles, have to be estimated, and the mutual inductive action of which may be considerable because of the large size of the C=O moment. Evidently, the situation in these molecules is somewhat analogous to that in the

glycols. The large mutual potential energies of the dipoles have little effect upon the resultant moment, so that the ethyl oxalate molecule has a moment practically the same as those of the very long molecules. It is only in the diethyl succinate molecule, where there is good reason to believe in the formation of a ring, that any considerable difference in moment occurs. The results justify the conclusion originally drawn that the long chains do not bend around upon themselves to form ring structures.

Summary

Equations have been derived for the calculation of the electric moments of molecules of various lengths, containing two, three and four dipoles which may move relatively to one another.

The moments of four polymethylene bromides, 1,2,3-tribromopropane, two chlorohydrins, a bromohydrin and two dihalogenated ethers have been determined and the results, together with previously measured values for the glycols, now slightly revised, are compared with the values calculated by means of the equations. It is shown that dipoles not far apart on a carbon chain affect one another's positions in such a way as to diminish the resultant moment of the molecule. The results for the liquids may be explained by supposing that free rotation about the C–C bonds gives a great variety of forms to long-chain molecules, some of which are excluded because of high mutual potential energies of the dipoles; but a more satisfactory explanation is given by the supposition of an extended zigzag structure of the carbon chain with complete freedom of rotation only at the ends of the chain. In these solutions, any considerable bending around of the polar molecules to form ring structures is excluded in most cases.

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