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The Dipole Moments and Structures of Certain Long-Chain Molecules

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The dipole moment of isoprene is measured and found to differ so little from zero that it cannot play a part in the tendency of the substance to polymerize. The moments of hexamethylene and nonamethylene bromide are determined and that of trimethylene bromide is redetermined. Consideration of these values with those previously measured for other long-chain dibromides indicates that the moment of trimethylene bromide may be increased by

the existence of a van der Waals attractive force between the two bromine atoms. The orienting effect of the two C—Br dipoles upon one another becomes negligibly small when the carbon chain between them is lengthened from six to nine atoms. The results are best explained by the supposition that the carbon chain is an extended zigzag structure which is not infrequently bent by rotation around one or more C—C bonds.

SINCE the completion of two series of measurements of the dipole moments of polymethylene bromides,¹ Professor C. S. Marvel of the University of Illinois has very kindly lent us samples of hexamethylene bromide and nonamethylene bromide, which are here used to fill the two most important gaps left in the data on the polymethylene bromides. Because of the importance of isoprene in the building up of complex molecules, it seems not inappropriate to include measurements on it with those on the two long-chain molecules. Through the kindness of Dr. Thomas Midgley, Jr., and of Dr. Albert L. Henne, a sample of isoprene prepared by the latter was obtained for the measurements. As a check upon the earlier work, trimethylene bromide was measured in heptane solution.

PURIFICATION OF MATERIALS

Heptane

Heptane was obtained as in earlier work.²

Isoprene

Isoprene was obtained from Dr. Albert L. Henne of Ohio State University as a mixture of 60 percent isoprene with amylenes. For its molecular weight a weighted mean, 68.87, was used. n_D^{25} 1.40995.

¹ C. P. Smyth and S. E. Kamerling, *J. Am. Chem. Soc.* **53**, 2988 (1931); C. P. Smyth and W. S. Walls, *ibid.* **54**, 2261 (1932).

² C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **54**, 1854 (1932).

Trimethylene bromide

The material used was some of that purified for earlier work,¹ possessing the same refractive index as at the time of the earlier measurements.

Hexamethylene bromide

A somewhat impure sample, b.p. 92–93° (3 mm) kindly lent by Professor C. S. Marvel of the University of Illinois was twice fractionally distilled under reduced pressure. After this material had been used for solutions the solvent was distilled off and the residual hexamethylene bromide was twice fractionally distilled under reduced pressure. A small sample of the middle fraction was used for making additional solutions, the polarizations of which checked those obtained for the first sample.

Nonamethylene bromide

A pure sample, b.p. 127–129° (7 mm) obtained from Professor Marvel was fractionally distilled slowly under reduced pressure, the middle fraction distilling at 103–105° (2 mm) being collected; n_D^{20} 1.49521.

EXPERIMENTAL RESULTS

The densities and dielectric constants of the solutions of the polar substances in the nonpolar were measured with the apparatus and methods previously employed,³ a wave-length of 1000 meters being used in the dielectric constant de-

³ C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **53**, 527 (1931).

terminations. 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 given opposite $c_2=0$ are those for the solvent. P_2 has been extrapolated to $c_2=0$ in the usual manner to obtain P_∞ , from which the moment is calculated as $\mu = 0.0127 \times 10^{-18} [(P_\infty - MR_D)T]^{\frac{1}{2}}$. MR_D , the molar refraction for the D sodium line, was determined directly for isoprene and trimethylene bromide and, for the two long-chain bromides, was calculated as the sum of the atomic refractions. The values of these quantities are given in Table II, and, in Table III, the moments obtained for these dibromides are listed with those previously obtained by Smyth and

TABLE I. Dielectric constants, densities and polarizations.

Heptane-isoprene (60%) + amylenes (40%) (Mean $M = 68.87$).						
c_2	ϵ 25°		d 25°		P_2 25°	
0.00000	1.920		0.6795		(34.58 = P_1)	
0.32132	1.959		.6770		27.27	
0.44984	1.978		.6760		27.29	
0.73520	2.028		.6737		27.30	
1.00000	2.087		.6715		27.28	

Heptane-trimethylene bromide.						
c_2	ϵ		d		P_2	
	25°	50°	25°	50°	25°	50°
0.00000	1.920	1.883	0.6795	0.6577	(34.58	34.62 = P_1)
.03248	2.025	1.978	.7089	.6865	114.0	109.1
.07650	2.178	2.114	.7499	.7267	113.0	107.7
.13707	2.406	2.314	.8080	.7836	111.0	105.5
.18568	2.603	2.490	.8563	.8312	109.0	104.1

Heptane-hexamethylene bromide.						
	ϵ	d	ϵ	d	P_2	P_2
	25°	50°	25°	50°	25°	50°
0.03148	2.065	2.014	0.7106	0.6884	162.0	155.0
.06780	2.239	2.174	.7467	.7239	158.9	153.6
.10946	2.447	2.365	.7877	.7643	155.9	151.5
.13438	2.579	2.485	.8123	.7886	154.8	150.2

(Middle fraction of recovered hexamethylene bromide.)						
	ϵ	d	ϵ	d	P_2	P_2
	25°	50°	25°	50°	25°	50°
0.02898	2.054	2.004	0.7082	0.6860	162.6	155.4
.05828	2.195	2.130	.7371	.7144	160.9	153.7
.05841	2.196	2.131	.7374	.7147	160.8	153.8

Heptane-nonamethylene bromide.						
	ϵ	d	ϵ	d	P_2	P_2
	25°	50°	25°	50°	25°	50°
0.02368	2.041	1.994	0.7033	0.6816	191.3	184.5
.04631	2.159	2.101	.7255	.7035	189.8	183.2
.06669	2.262	2.195	.7452	.7229	186.5	180.4
.09153	2.393	2.313	.7689	.7464	184.6	178.4
.09891	2.429	2.346	.7757	.7532	183.3	177.3

TABLE II. Refractions, orientation polarizations and electric moments.

	MR_D	$P_\infty - MR_D$ 25° 50°	$\mu \times 10^{18}$ 25° 50°	
Isoprene (60%) + amylenes (40%)	25.41	1.87	(0.3)	
Trimethylene bromide	31.2	84.8	79.0	2.02 2.03
Hexamethylene bromide	45.3	119.0	111.4	2.39 2.41
Nonamethylene bromide	59.3	135.2	128.2	2.55 2.58

TABLE III. Dipole moments of polymethylene bromides.

Compound	Formula	Solvent	$\mu \times 10^{18}$ 25° 50°	
Ethylene bromide	Br(CH ₂) ₂ Br	Heptane	1.02	1.05
Ethylene bromide		Benzene	1.50	1.52
Trimethylene bromide	Br(CH ₂) ₃ Br	Heptane	2.02	2.03
Trimethylene bromide		Benzene	1.97	1.98
Tetramethylene bromide	Br(CH ₂) ₄ Br	Heptane	1.96	2.01
Tetramethylene bromide		Benzene	2.00	2.03
Pentamethylene bromide	Br(CH ₂) ₅ Br	Benzene	2.25	2.28
Hexamethylene bromide	Br(CH ₂) ₆ Br	Heptane	2.39	2.41
Nonamethylene bromide	Br(CH ₂) ₉ Br	Heptane	2.55	2.58
Decamethylene bromide	Br(CH ₂) ₁₀ Br	Benzene	2.54	2.56

Kamerling for ethylene bromide and by Smyth and Walls for the higher dibromides.

DISCUSSION OF RESULTS

Although the formula of isoprene, $\text{CH}_2=\text{CH} \cdot \text{C}(\text{CH}_3)=\text{CH}_2$, gave reason to expect a moment too small to detect by means of measurements on the liquid, it seemed desirable to establish beyond all doubt that its ease of polymerization was not caused by the moment of the molecule as a whole. The apparent mean moment, 0.3×10^{-18} , found for the mixture of isoprene and amylenes is so small that it may arise entirely from neglect of the atomic polarization. The fact that propylene⁴ and α -butylene⁵ have moments of 0.37×10^{-18} , while ethylene⁵ has zero moment, shows that the double bond itself has no dipole moment, although it may give rise to a moment if unsymmetrically placed in a molecule. The maximum moment to be expected of an amylenes is evidently about 0.4×10^{-18} and the mixture would, doubtless, have a decidedly smaller moment. The experimental result shows

⁴ K. B. McAlpine and C. P. Smyth, unpublished measurements.

⁵ C. P. Smyth and C. T. Zahn, J. Am. Chem. Soc. **47**, 2501 (1925).

a mean moment for the isoprene-amylenes mixture between 0 and 0.3×10^{-18} and, therefore, a moment for isoprene lying between approximately the same limits, as would be predicted from the fact that the small moments arising from the double bonds at each end of the molecule would partially cancel one another. It is evident, therefore, that the dipole moment of the molecule is too small to play any appreciable part in the tendency toward polymerization.

The moment of a polymethylene bromide molecule may, as a fair approximation, be regarded as the resultant of the moments in the two C—Br lines and is thus dependent upon the mutual orientation of these bonds. The difference between the moment of ethylene bromide in heptane and in benzene has been attributed to the weakening by the benzene of the forces between the two C—Br dipoles, which, by lessening the potential energy between the dipoles, permits of their turning about the C—C axis farther out of the trans position.⁶

The large energy due to the close proximity of the bromine atoms in the small molecule tends to keep the dipoles near this trans position, thus causing the moment of ethylene bromide to be much lower than the moments of the longer dibromides. Since, in the cases of trimethylene and tetramethylene bromide, the moments are almost the same in the two solvents, it appears safe to neglect the difference of solvent in the case of the longer molecules, where the effect of solvent should be even less. It was shown in the earlier work that, with one exception, the moments could be satisfactorily explained by the assumption of freedom of rotation about all 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 being less probable in the shorter molecules and the moments, consequently, being smaller than the calculated values, the difference between observed and calculated values lessening as increasing length of the chain lessens the mutual potential energy of the two dipoles. However, the closeness of the moment of tetramethylene bromide to that of trimethylene bromide was

not accounted for by this explanation. It was pointed out that, if the carbon chain retained a rigid zigzag structure with freedom of rotation only about the end C—C bonds, the molecules with an even number of carbon atoms in the chain should have a moment 0.1×10^{-18} lower than those with an odd number of carbons. This would reduce the rise in moment from the three-carbon to the four-carbon compound caused by increasing separation of the two dipoles and thus keep the values close together. In similar fashion, the moments of the five- and six-carbon compounds should be close together, but the moment of hexamethylene bromide, now available to test the hypothesis, is decidedly higher than that of pentamethylene bromide. Because of its greater length, the six-carbon chain offers greater opportunity for some departure from the rigid zigzag structure than does the four-carbon chain, but the marked difference between the moments of the five- and six-carbon compounds renders improbable an explanation of the closeness of the three- and four-carbon values in terms of an alternating effect caused by a rigid zigzag chain.

In our earlier paper, the mutual potential energies of the two dipoles in the different molecules were considered, but discussion of the energies due to other interatomic forces was postponed. Eyring⁷ has treated such forces in calculating the dependence of the potential energy of the ethane molecule on rotation about the C—C bond. In the present case, in addition to the forces between the dipoles, which affect their positions relative to one another in such a way as to reduce the resultant moment, there is a repulsive potential, such as $R^n e^{-\beta R}$, which vanishes for distances R appreciably greater than kinetic theory diameters and a van der Waals potential, $-C/R^6$, which gives rise to attraction.

The constant C for an atom is easily calculated by the method of London.⁸ In trimethylene bromide, rotation around the two C—C lines, which make an angle of 110° with each other, would cause the distance between the bromine nuclei to vary from about 6Å down to that of the

⁶ C. P. Smyth, R. W. Dornte and E. Bright Wilson, Jr., *J. Am. Chem. Soc.* **53**, 4242 (1931).

⁷ H. Eyring, *J. Am. Chem. Soc.* **54**, 3191 (1932).

⁸ F. London, *Zeits. f. physik. Chemie (B)* **11**, 222 (1930).

closest possible approach of the two atoms to each other. If the two atoms lay in the same plane on the inside of the C—C—C angle, the nuclear separation of the two bromines would be only 1.53Å. As this distance is considerably smaller than the diameter of a bromine atom,⁹ it is evident that this position and positions close to it are impossible in the trimethylene bromide molecule. As these are positions in which the two dipoles are not far from pointing in the same direction and thus giving a large moment to the molecule as a whole, it is evident that the moment observed for the molecule will be considerably smaller than that calculated on the assumption that all positions of rotation around the two C—C lines are equally probable. On the other hand, when the internuclear separation is a little greater than the kinetic theory diameter for the bromine atom, the van der Waals potential will become more important than the repulsive potential and there will be an attractive force between the bromine atoms, tending to overcome the repulsion between the dipoles pointing more or less in the same direction. There should, therefore, be a value of the internuclear separation at which the attractive and repulsive forces should approximately compensate one another. The dipoles would then oscillate about this position of minimum potential energy rather than about that in which the two point in opposite directions to give zero moment to the molecule and a minimum dipole potential energy.

The compensation between the repulsive and attractive forces of the bromine atom in the absence of dipole forces is shown by liquid bromine, in which calculation from the density shows that the average volume occupied by a molecule at 0° is equal to that of a cube with an edge of 4.35Å. In terms of the dimensions given by Pauling, the Br₂ molecule would be roughly a cylinder of diameter 2.28Å with hemispherical ends and total length 4.56Å. These dimensions are, of course, decidedly smaller than those given by kinetic theory, from which Smyth and Rogers¹⁰ calculated a diameter 3.2Å for the bromine atom. This would extend the hypo-

thetical surface of the molecule calculated from the Pauling dimensions to a distance of 1.6Å from the line joining the two bromine nuclei. If the liquid is regarded as made up of molecules of this shape packed parallel to one another in layers, it may be calculated that the average separation of the nearest bromine nuclei in adjacent molecules is about 3.6Å. This very rough figure indicates a distance just above which the van der Waals attractive forces should tend to compensate the dipole repulsive forces in trimethylene bromide and give a point of minimum energy for the dipoles. With the bromines at such distances apart in the molecule, the dipoles make such angles with one another as to give considerable resultant moments to the molecules. This should cause the observed moment to be nearer that calculated on the basis of equal probability for all positions of rotation than would be expected in view of the shortness of the carbon chain. In other words, it is not that the tetramethylene bromide moment is low as previously supposed, but that the trimethylene bromide moment is unexpectedly high.

Although the van der Waals attraction may play a part in the tetramethylene bromide molecule, it must be a small part unless the carbon chain is distorted enough by rotation around the C—C bonds to bring the bromines close together. It seems probable that only in trimethylene bromide are the distances between the bromines commonly of such a size as to make the van der Waals attraction between them important. It is also of interest to note that, if the two dipoles in trimethylene bromide are oscillating about a position in which the resultant of their two moments is considerable, increased oscillation accompanying rising temperature will not greatly affect the observed moment. Actually, the values in Table III show a negligible increase in moment from 25° to 50°, and the earlier and less accurate determinations by Smyth and Kamerling showed an apparent increase in moment with temperature decidedly smaller for trimethylene bromide than for pentamethylene.

Since the van der Waals potential varies inversely as the sixth power of the distance, it is negligible in the molecules containing more than

⁹ L. Pauling, Proc. Nat. Acad. Sci. 18, 293 (1932).

¹⁰ C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. 52, 2227 (1930).

four carbons unless the ends of the chain are brought close together through rotation around the C—C lines. However, the potential energy between the two dipoles, which varies inversely as the cube of the distance, is still not inconsiderable when they are separated by a rigid zigzag chain of five carbon atoms. In connection with our earlier paper, it was calculated that the potential energy between the two dipoles when both were pointing upward in a sort of cis position was 1×10^{-14} erg greater than when one pointed downward in the opposite direction as in a trans position. As this difference is approximately $1/4 kT$, it was evident that the trans position of zero moment was the more probable and that the observed moment would still be lower than the calculated and would show some increase with temperature as observed by Smyth and Kamerling. As the separation of the dipoles was approximately doubled in decamethylene bromide, it was evident that the difference between the potential energies of the cis and trans positions was about $1/8$ of that in pentamethylene bromide, or about $1/32 kT$, an energy too small to have any appreciable orienting effect upon the dipoles. In conformity with this, the observed moment was found to differ by less than the uncertainty of the calculation from the value calculated on the assumption of the equal probability of all positions of rotation, and was further found to show little or no variation with temperature.

The approximate validity of the potential energy calculation receives striking confirmation from the additional moments in Table III. The moment of hexamethylene bromide is higher than that of pentamethylene because the dipoles are farther apart and have, therefore, a lower mutual potential energy. However, the difference in potential energy between the cis and trans positions is still not wholly negligible in comparison to kT and is still, therefore, sufficient to make a little less probable the cis positions, which have greater moment, the resultant moment of the molecule, consequently, being

somewhat below the calculated value. In nonamethylene bromide, however, the difference in potential energy between the cis and trans positions is so small in comparison to kT as to produce no lowering of the moment, which is practically identical with that of decamethylene bromide and in satisfactory agreement with the calculated value. In the calculation of the resultant moment of the two dipoles, a moment of 1.9×10^{-18} was assigned to each dipole and located in the C—Br line 1.7 Å from the carbon nucleus. The location of the moments is a rough approximation which makes approximate the calculation of the potential energy between them. In hexamethylene bromide the difference in potential energy between the cis and the trans position is about $1/7 kT$, which is evidently still sufficient to have a small orienting effect on the dipoles. The difference in nonamethylene bromide drops to about $1/23 kT$, which, as would be expected, is evidently insufficient to produce detectable orientation.

It must be concluded that the moments in Table III give no positive evidence of an alternating effect such as might be expected if the carbon chain were a rigid zigzag structure, although, in the earlier work, the seemingly low moment of tetramethylene bromide was regarded as an indication of such a structure. However, the small difference, 0.1×10^{-18} , calculated between the molecules with an even-numbered carbon chain and those with an odd would be lessened by any bending of the chain and more or less obscured by the lowering of the moment because of the mutual potential energies of the dipoles and because of inductive effects. Although, as pointed out in the earlier work, the moments do not decide definitely between an extended zigzag carbon chain and one in which free rotation around the C—C bonds gives a great variety of forms to the chain, the results are best explained by the supposition of an extended zigzag chain which is not infrequently bent by rotation around one or more links in the chain.