TABLE II

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES FOR GASEOUS PROPANE (C_3H_8)

For each temperature the first line gives the observed pressure and the second line the observed minus the calculated pressure. The calculated pressures are computed from the equation given in Table I. The critical constants of propane are: t_c = 96.81° (Int.); p_c = 42.01 normal atmospheres; d_c = 5.13 moles per liter, and v_c = 0.195 liter per mole.[2]

Density, moles/liter		1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5	6	7	8	9	10
Temp., °C. (Int.)							Pressure, normal atmospheres.								
96.81	obsd.	23.35	30.68	35.82		40.76		41.93		42.04	42.15	44.14	54.86	88.89	171.09
	obsd.-calcd.	−0.38	−0.52	−0.46		−0.14		+0.97		+2.06					
100	obsd.	23.77	31.30	36.56	40.05	42.15	43.31	43.92	44.24	44.46	45.16	48.27	60.70	96.84	181.42
	obsd.-calcd.	−0.28	−0.42	−0.48	−0.35	−0.07	+0.39	+0.97	+1.50	+1.72					
125	obsd.	26.42	35.64	42.79	48.30	52.59	56.01	58.87	61.49	64.11	70.72	82.73	108.04	162.47	270.12
	obsd.-calcd.	−0.13	−0.19	−0.17	−0.05	+0.17	+0.42	+0.59	+0.57	+0.14					
150	obsd.	28.97	39.79	48.74	56.23	62.60	68.24	73.47	78.61	84.02	97.39	118.62	156.94	228.77	
	obsd.-calcd.	−0.08	−0.10	−0.06	+0.05	+0.17	+0.26	+0.24	±0.00	−0.54					
175	obsd.	31.47	43.86	54.57	63.97	72.42	80.30	87.95	95.73	104.06	124.52	155.19	206.31	294.77	
	obsd.-calcd.	−0.05	−0.05	−0.01	+0.07	+0.13	+0.15	+0.07	−0.18	−0.60					
200	obsd.	33.95	47.87	60.28	71.57	82.38	92.21	102.30	112.79	124.12	151.85	192.28	256.10		
	obsd.-calcd.	−0.04	−0.05	−0.03	+0.02	+0.35	+0.07	±0.00	−0.11	−0.25					
225	obsd.	36.41	51.83	65.94	79.08	91.66	104.02	116.58	129.79	143.21	179.24	229.08	305.78		
	obsd.-calcd.	− .04	−0.07	−0.06	−0.04	±0.00	+0.02	+0.05	+0.14	−0.55					
250	obsd.	38.77	55.63	71.53	86.53	101.14	115.74	130.79	146.75	163.19	206.67	266.06			
	obsd.-calcd.	−0.13	−0.23	−0.12	−0.12	−0.08	±0.00	+0.19	+0.56	+0.30					
275	obsd.	41.23	59.64	77.08	93.91	110.54	127.38	145.02	163.64	184.25	234.08	303.03			
	obsd.-calcd.	−0.11	−0.17	−0.20	−0.22	−0.17	−0.01	+0.47	+1.08	+2.44					
Average deviation, atm.		0.138	0.200	0.177	0.115	0.142	0.165	0.394	0.518	0.956					
Average % deviation		0.509	0.540	0.411	0.204	0.214	0.291	0.717	0.719	1.366					

Total average deviation, 0.313 atm.; Total average % deviation, 0.558.

0.2% at 125°, 0.3% at 150°, and 0.4% at 175°. The differences did not depend on density but on temperature alone. Only the data of run two are reported.

Results

The compressibility data are given in Table II. The constants of the Beattie–Bridgeman equation of state were determined from the data below the critical density and the constants for propane are given in Table I. The comparison of the pressures computed from the equation with the observed pressures is given in Table II. The agreement is fair.

Summary

Measurements are reported on the compressibility of gaseous propane over the temperature range 96.81 to 275° and from a density of 1.0 to 10.0 moles per liter.

The values of the constants of an equation of state are determined from the data for densities less than the critical.

CAMBRIDGE, MASS.

RECEIVED MAY 11, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Electric Moments of Some Dioxanes and Dioxolanes

BY M. M. OTTO

In a previous article[1] moments were determined for compounds containing two oxygen atoms attached to one carbon atom. The other valence bonds of the oxygens were satisfied with aliphatic groups, each of which was independent of the other. It should be interesting to find the effect of combining the two oxygen atoms with a carbon group to form a ring compound. Such substances as the dioxanes and dioxolanes would fulfil the requirement and therefore moments were determined for these compounds.

Preparation of Compounds and Apparatus.—The 2,2-dimethyl-1,3-dioxolane was made from acetone and ethylene glycol[2] using *p*-toluenesulfonic acid as a catalyst. The 2-bromomethyl-1,3-dioxolane and 2-bromomethyl-1,3-dioxane were prepared[3] from bromoacetaldehyde and ethylene

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(1) Otto, THIS JOURNAL, **57**, 693 (1935).

(2) R. Leutner, *Monatsh.*, **60**, 317 (1932).

(3) Hill, THIS JOURNAL, **50**, 2729 (1928).

glycol or trimethylene glycol, respectively. The remainder of the compounds were made from the appropriate acetylene and glycol using boron fluoride and mercuric oxide as catalyst.[4]

TABLE I

BOILING POINT, DENSITY, AND REFRACTIVE INDEX OF COMPOUNDS

	B. p., °C.	d^{25}	$n^{25}D$
2-Methyl-1,3-dioxolane	83	0.97494	1.39484
2,4-Dimethyl-1,3-dioxolane	93	.92251	1.39251
2,4,4,5,5-Pentamethyl-1,3-dioxolane	133	.99560	1.41048
2,2-Dimethyl-1,3-dioxolane	91–92	.93714	1.39621
2-Methyl-1,3-dioxane	109	.96455	1.41147
2-Methyl-2-amyl-1,3-dioxane	88 at 10 mm.	.90768	1.43380
2-Bromomethyl-1,3-dioxolane	63–64, 13 mm.	1.6231	1.48056
2-Bromomethyl-1,3-dioxane	96–97, 26 mm.	1.5279	1.48348

TABLE II

DIELECTRIC CONSTANT AND DENSITIES OF SOLUTIONS

C_2	d^{25}	ϵ
2-Methyl-1,3-dioxolane		
0.03543	0.87559	2.3363
.05984	.87825	2.3766
.08943	.88112	2.4263
.1305	.88544	2.4977
2,4-Dimethyl-1,3-dioxolane		
0.04456	0.87497	2.3598
.06766	.87640	2.4025
.08524	.87759	2.4360
.11086	.87915	2.4842
2,4,4,5,5-Pentamethyl-1,3-dioxolane		
0.03569	0.87254	2.3392
.05208	.87312	2.3688
.06313	.87338	2.3892
.07961	.87385	2.4179
2,2-Dimethyl-1,3-dioxolane		
0.04200	0.87541	2.3286
.07094	.87739	2.3661
.09191	.87884	2.3941
.11910	.88070	2.4286
2-Methyl-1,3-dioxane		
0.02404	0.87502	2.3881
.04690	.87726	2.4941
.06755	.87934	2.5903
.09782	.88291	2.7376
2-Methyl-2-amyl-1,3-dioxane		
0.03884	0.87491	2.4539
.05046	.87565	2.5068
.06093	.87635	2.5558
.07635	.87747	2.6257
2-Bromomethyl-1,3-dioxolane		
0.03409	0.90112	2.5227
.04526	.91089	2.6032
.05727	.92124	2.6898
2-Bromomethyl-1,3-dioxane		
0.02660	0.89477	2.5869
.04109	.90716	2.7531
.04904	.91413	2.8433
.05451	.91872	2.9175

The physical constants of the compound are listed in Table I. The dielectric constants were determined using the apparatus previously described.[5] Density and refractive index were determined as before.[6] Polarization at infinite dilution (P_∞) was calculated by method of preceding article.[1] Table II lists the data necessary for the calculation of polarization at infinite dilution (P_∞). Molecular refraction (MR_D) and electric moment (μ) are tabulated in Table III.

TABLE III

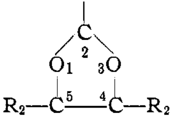
POLARIZATIONS AND ELECTRIC MOMENTS

Compound	P_∞	MR_D	$10^{18}\mu$
2-Methyl-1,3-dioxolane	51.90	21.65	1.21
2,4-Dimethyl-1,3-dioxolane	62.22	26.32	1.32
2,4,4,5,5-Pentamethyl-1,3-dioxolane	74.59	40.16	1.29
2,2-Dimethyl-1,3-dioxolane	51.48	25.59	1.12
2-Methyl-1,3-dioxane	100.05	26.30	1.89
2-Methyl-2-amyl-1,3-dioxane	124.09	49.37	1.90
2-Bromomethyl-1,3-dioxolane	136.74	29.25	2.28
2-Bromomethyl-1,3-dioxane	206.76	33.85	2.89

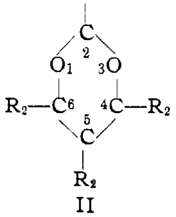
Discussion

In the dialkoxyalkanes[1] there is a possibility of rotation about C–O bonds which is not present in the dioxanes or dioxolanes. It would be expected that there would be an increase in moment in passing from a chain compound to a ring compound as the decrease in moment due to trans position of the oxygen atoms in chain compounds would not be present. That this is experimentally true may be perceived when the moments of the dialkoxyalkanes of about 0.90D are compared with the values of the dioxanes and dioxolanes in Table III.

A rather surprising result is obtained when the moments of the five-membered rings, the dioxolanes (I), are compared with the moments of the six-membered rings, the dioxanes (II). The dioxanes have a greater moment by about 0.57D.



I



II

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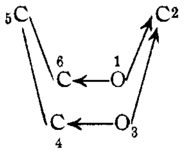
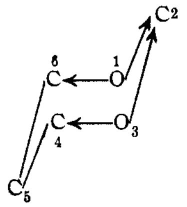
[4] Nieuwland, Vogt and Foohey, THIS JOURNAL, **52**, 1018 (1930).

[5] Otto, *ibid.*, **57**, 1476 (1935).

[6] Otto and Wenzke, *ibid.*, **56**, 1314 (1934).

The five-membered ring has probably almost a plane structure, which would be the case if the atoms involved in the ring had valence angles corresponding to those of a tetrahedral structure. It is not possible to construct a six-membered ring with a plane structure using tetrahedral forms for component atoms. If, however, the ring is distorted by rotation around valence bonds, or puckered, it is possible to construct a ring with the same valence angles. The structure could be either of the two structures illustrated below or an equilibrium mixture of the two in which the carbon atoms 2 and 5 are in a plane different from that of the other four atoms.





For the explanation here desired it should make little difference which of the forms is present, for the principal contribution to the moment comes from moments of the two oxygen atoms.

In the five-membered ring the resultant of the bond moments of the two oxygens attached to one carbon would be in the same plane as that of the resultant of the other component moments of the oxygen atoms. In the six-membered rings the two resultants would be in different planes and therefore the component of one resultant in the plane of the other would be less than if in the same plane. It is conceivable then that the total moments should be greater for the six-membered ring than for the five-membered ring as the two component moments of the oxygen and consequently the resultants of the moments of the two oxygens tend to oppose each other as illustrated by arrows in the figure.

This explanation should hold also if it were possible for one oxygen atom to be out of the plane of the four other atoms, as then the two resultant oxygen moments still would be in different planes.

Moments for 2-bromomethyl-1,3-dioxolane and 2-bromomethyl-1,3-dioxane were measured to test further the value of different sizes of ring moments. It is granted that the moment of the carbon to bromine bond is not in the same plane as the ring but its effect should be similar for both. As the moment is quite large there can be no great uncertainty of the atomic polarization. Table III shows that the five-membered ring compounds have smaller moments than the six-membered rings.

Substitution of methyl groups on the carbon after the first one is added other than the one attached to the two oxygens has little effect on the moment. Addition of another methyl group to the other carbon atom seems to lower the moment. This might be due to a more symmetrical molecule being formed.

Summary

1. Six-membered ring compounds containing two oxygens, dioxanes, have a larger moment than corresponding moments of five-membered rings, dioxolanes.

2. Electric moments have been determined for 2-methyl-, 2,4-dimethyl-, 2,4,5-trimethyl-, 2,4,4,5,5-pentamethyl-, 2,2,-dimethyl-, and 2-bromomethyl-1,3-dioxolane. Also moments were determined for 2-methyl-, 2-methyl-2-amyl-, and 2-bromomethyl-1,3-dioxane.

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