33. *The Dipole Moments of Vapours. Part III. Homologous Series.*

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In continuation of our work on the dipole moments of vapours we have now examined the first four or five members of a number of homologous series. Our main object was to study the induction along a hydrocarbon chain, which had already been discussed for such series from measurements made on solutions (cf. Cowley and Partington, J., 1933, 1253; 1935, 604).

The values we have found for the moments are compared with those of other observers (where these are available) in Table I. In calculating the dipole moment we have taken P_A as 5% of P_E measured for the sodium line, and have recalculated the data of other workers on this basis. In some cases this brings about a considerable change. Thus Sänger, Steiger, and Gächter (*Helv. Physica Acta*, 1932, **5**, 200) find for *n*-propyl chloride $\mu = 2{\cdot}04$* from the slope of the *P–T* curve, with $P_{A+E} = 25{\cdot}3$ c.c. Since $P_E = 20{\cdot}3$ this gives the rather large value 5·0 c.c. for P_A; P_A being taken as 1·0 c.c., the value of μ becomes 2·10, which agrees well with the values we have found for the butyl and the amyl compound. Since a very small error in *P* can cause a much larger error in the slope, we think it is better in comparing the moments of a series of compounds to avoid such errors by using a definite hypothesis as to the magnitude of P_A. It will be seen from Table I that our results are in good agreement with those of other workers for methyl bromide and iodide and for a number of other substances. Some of the data in the literature, however, diverge widely from our results or those of more recent investigators; these are enclosed in parentheses in the table and are neglected in calculating the most probable value of μ given in the third column. The last column gives the difference in moment, $\Delta\mu = \mu_{RX} - \mu_{CH_3X}$.

* All moments are given in Debye units (e.s.u. × 10^{-18}).

TABLE I.

Substance.	μ, obs.	Mean μ.	$\Delta\mu$.
CH_3Cl	1·87,[5] 1·88,[6] 1·86,[3] (1·69) [1]	1·87	—
C_2H_5Cl	2·06,[5] 2·06,[6] 2·04,[3] (2·11) [1]	2·05	+0·18
n-C_3H_7Cl	2·10 [6]	2·10	+0·23
n-C_4H_9Cl	2·11 [8]	2·11	+0·24
n-$C_5H_{11}Cl$	2·12 [8]	2·12	+0·25
CH_3Br	1·79,[8] 1·82,[1] 1·79 [2]	1·80	—
C_2H_5Br	2·01,[8] 2·02,[3] (2·09),[1] (1·78) [2]	2·01	+0·21
n-C_3H_7Br	2·15,[8] 2·11,[1] (1·79) [2]	2·13	+0·33
n-C_4H_9Br	2·15 [8]	2·15	+0·35
CH_3I	1·64,[8] 1·66,[1] 1·62 [2]	1·64	—
C_2H_5I	1·87,[8] (2·00),[1] (1·62) [2]	1·87	+0·23
n-C_3H_7I	2·01,[8] (1·63) [2]	2·01	+0·37
n-C_4H_9I	2·08 [8]	2·08	+0·44
$CH_3{\cdot}CN$	3·94,[8] 3·94 [1]	3·94	—
$C_2H_5{\cdot}CN$	4·03,[8] 4·05 [1]	4·04	+0·10
n-$C_3H_7{\cdot}CN$	4·05 [8]	4·05	+0·11
n-$C_4H_9{\cdot}CN$	4·09 [7]	4·09	+0·15
$CH_3{\cdot}NO_2$	3·54,[8] (3·48),[4] (3·78) [1]	3·54	—
$C_2H_5{\cdot}NO_2$	3·58,[8] (4·03) [1]	3·58	+0·04
n-$C_3H_7{\cdot}NO_2$	3·57 [8]	3·57	+0·03
n-$C_4H_9{\cdot}NO_2$	3·55 [8]	3·55	±0·01
$CH_3{\cdot}OH$	1·71,[9] 1·68 [10]	1·69	—
$C_2H_5{\cdot}OH$	1·68,[9] 1·70,[10] 1·69 [11]	1·69	±0·00
n-$C_3H_7{\cdot}OH$	1·64,[9] 1·66 [10]	1·65	−0·04
n-$C_4H_9{\cdot}OH$	1·63,[9] 1·66 [10]	1·65	−0·04

References.—[1] Højendahl, Thesis, Copenhagen, 1928. [2] Mahanti, *Physikal. Z.*, 1930, **31**, 548. [3] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499. [4] *Idem*, *J. Amer. Chem. Soc.*, 1934, **56**, 1697. [5] Fuchs, *Z. physikal. Chem.*, 1930, **63**, 824. [6] Sänger, Steiger, and Gächter, *loc. cit.* [7] Groves and Sugden, J., 1935, 971. [8] *Idem*, this paper. [9] Kobu, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1935, **26**, 242; **27**, 65. [10] Miles, *Physical Rev.*, 1929, **34**, 964. [11] Knowles, *J. Physical Chem.*, 1932, **36**, 2554.

Inspection of the figures makes it clear that the change in the moment of a compound R–X as the group R increases depends upon other factors than simple induction along the hydrocarbon chain. In the first place, it is evident that the nature of the group X plays an important part. This is well shown by the data for the alkyl halides which all have dipole moments of the same order of magnitude; if the effect is due to induction in the growing chain by a dipole of infinitely small length situated between the carbon and halogen atoms, these three series should all show much the same effect. It will be seen, however, that, whilst the chlorides show practically no increase in moment after the propyl compound, the iodides show a much larger increase in moment as the series is ascended, and a limit has not been reached at the butyl compound. The bromides show an intermediate behaviour; methyl bromide has a smaller moment than methyl chloride, whilst *n*-butyl bromide has a distinctly larger moment than the chloride.

Similarly, the nitro-paraffins and the nitriles, which have much larger moments than the halides, show a very small influence of the size of the radical on the dipole. With the nitro-paraffins the moment is constant from the methyl to the butyl compound within the experimental error. When comparing these compounds with the halides it must be remembered that the dipole is situated one atom further away from the growing alkyl chain, so that the Me — Et difference in the nitriles should be compared with the Et — Pr difference in the iodides. (This is true for the nitriles, but with the nitro-paraffins the C–N link which is adjacent to the growing radical has a considerable moment and should largely determine the induction.)

The theory of induction by dipoles has recently been developed by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) and by Higasi (*Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1936, **28**, 284) with special reference to the influence of solvents on the values found for moments in solution. Their conclusions can be applied to discuss the influence of the addition of non-polar groups to a polarised molecule when the moment is measured in the gaseous phase, and Frank discusses the " radical effect " in some detail.

If the molecule can be regarded as bounded by a surface of revolution about the axis of the dipole, then, by symmetry, the components of the induced moments normal to the dipole axis cancel out. The sign of the component parallel to the primary dipole depends upon the position of the polarisable part of the molecule with respect to the dipole axis. Frank shows that the induced component in any element of polarisable matter which is situated within two cones of semi-angle 55° about the axis of the dipole axis will be in the same direction as the primary dipole and will augment the measured moment. Elements situated outside these cones will have moments induced in them which will oppose the primary dipole and will diminish the measured moment. Methods of computing the magnitude of the induced dipoles are given by Frank and by Higasi; for our present purpose, however, a qualitative discussion will be sufficient.

In a homologous series it is evident that the growing carbon chain will in general, when vibrations and rotations are taken into account, add polarisable matter in a region in which the induced moment will be in the same sense as the primary dipole; an increase in moment should therefore be found on ascending any such series. Furthermore, the value of $\Delta\mu/\mu$ should be the same in all series where $\Delta\mu$ is the increase on passing from the first to the nth carbon atom and μ is the primary moment. It is clear from the data in Table I that the experimental values do not agree with these conclusions.

Frank (*loc. cit.*) notes that the theoretical treatment of the problem assumes (*a*) that the field distribution due to primary dipole is not altered by the introduction of polarisable matter in its vicinity, and (*b*) that the dipole is of negligible length. These approximations may not lead to serious errors in computing solvent effects but become important for the discussion of the effect of radicals on moments measured in the gaseous phase.

From the data obtained in the present investigation it appears that the polarisability of the group X plays an important part. In the methyl halides, for example, part of the halogen atom subtending an angle of more than 55° from the dipole axis is situated in a region of intense field and will be strongly polarised in a sense which will oppose the primary dipole. (This effect will be enhanced if the dipole is assumed to have a finite length or if the dipole is supposed to be embedded in the halogen atom. The dipole model is, however, but a crude approximation to the distribution of electrical charges within a molecule, so that a detailed analysis would be out of place at the present stage of our knowledge.) The addition of more CH_2 groups provides an easier path for the lines of force on the side of the molecule remote from the halogen atom, the electrical strain on the part of the halogen atom nearest the dipole will be diminished and the moment of the molecule will increase. A redistribution of the electric field as the length of the carbon chain increases can in this way produce an increase in moment along a homologous series of halides, and in particular, accounts for the order $Cl < Br < I$.

The moments found for substances in which the polar group is attached to a branched chain can also be accounted for by a redistribution of electric field. The data for some normal and branched-chain compounds are compared in Table II.

TABLE II.

Effect of Chain Branching.

Substance.	μ.	Substance.	μ.	Substance.	μ.
n-C_3H_7Cl	2·10 [6]	*n*-$C_3H_7{\cdot}OH$	1·65 [9, 10]	*n*-C_4H_9Br	2·15 [8]
iso-C_3H_7Cl	2·15 [8]	*iso*-$C_3H_7{\cdot}OH$...........	1·63 [9]	*sec.*-C_4H_9Br	2·20 [8]
n-C_3H_7Br...............	2·13 [8, 1]	*n*-$C_4H_9{\cdot}OH$	1·65 [9, 10]		
iso-C_3H_7Br	2·19 [8]	*iso*-$C_4H_9{\cdot}OH$...........	1·60 [9]		

(For references see Table I.)

It will be seen that the halides which have the structure ${}^{C}_{C}\!\!>\!CX$ possess a higher moment than the isomeric normal compounds. Branching of the chain at the carbon atom to which the polar group is attached brings more polarisable matter into the neighbourhood of the dipole and should produce a greater relaxation of the field on the halogen atom than occurs with the corresponding normal compound. On the other hand, if field redistribution is neglected, then on Frank's theory chain branching would bring part of the alkyl group into the region in which the induced moment is zero or negative, and a small decrease in moment would be expected.

Finally, the data for some alcohols which are included in Tables I and II show a small decrease in moment on ascending a homologous series and a small decrease on passing from a normal to an *iso*-compound. The effect is not much larger than the experimental error and obviously requires further experimental study.

EXPERIMENTAL.

The polarisations of the vapours were measured with the apparatus described in Part I (J., 1934, 1094). In the tables below, T is the absolute temperature, p the pressure of the vapour in mm. Hg, P the measured polarisation in c.c., and μ the dipole moment deduced on the assumption that P_A is 5% of P_E. All the values given for P_E refer to the Na-D line.

iso*Propyl chloride* (b. p. 35·5°/757 mm.; $d_{4^\circ}^{20^\circ}$ 0·8610; I.C.T. give $d_{4^\circ}^{20^\circ}$ 0·860); $P_E = 20{\cdot}3$.

T.	p.	P.	μ.	T.	p.	P.	μ.	T.	p.	P.	μ.
288°	109	121·6	2·16	354°	184	103·1	2·16	383°	124	95·0	2·13
,,	108	122·0	2·16	,,	120	102·5	2·15	,,	186	96·4	2·15

Mean 2·15 ± 0·01.

n-*Butyl chloride* (b. p. 77·6°/748 mm.; $d_{4^\circ}^{20^\circ}$ 0·8845; I.C.T. give $d_{4^\circ}^{20^\circ}$ 0·884); $P_E = 25{\cdot}4$.

288	54	122·4	2·11	335	77	109·7	2·12	375	73	100·2	2·11
,,	52	122·9	2·12	,,	68	108·9	2·11	,,	73	100·2	2·11

Mean 2·11 ± 0·01.

n-*Amyl chloride* (b. p. 106·3°/771 mm.; $d_{4^\circ}^{20^\circ}$ 0·8879; Karvonen, *Ann. Acad. Sci. Fenn.*, *A*, **5**, No. 6, 123, gives $d_{4^\circ}^{20^\circ}$ 0·88715); $P_E = 30{\cdot}3$.

351	95	111·6	2·13	381	138	104·3	2·11
,,	102	111·2	2·12	,,	110	105·2	2·13

Mean 2·12 ± 0·01.

At higher temperatures the moment suddenly increased to about 2·20—2·24. This may be due to rearrangement to *sec.*-amyl chloride.

Methyl bromide. [A commercial specimen was allowed to evaporate spontaneously at room temperature and the middle third collected and used for the measurements. During fractionation the b. p. remained steady at 4·5°/755 mm.] P_E (calc. from data for homologues) $= 14{\cdot}5$.

291	140	83·7	1·80	335·5	130	74·2	1·79	363	165	70·0	1·79
,,	130	82·1	1·78	,,	187	73·4	1·78	,,	196	70·0	1·79
416	250	63·5	1·80	416	220	63·0	1·79				

Mean 1·79 ± 0·01.

Ethyl bromide (b. p. 38·4°/761 mm.; $d_{4^\circ}^{20^\circ}$ 1·4599; I.C.T. give $d_{4^\circ}^{20^\circ}$ 1·4602); $P_E = 19{\cdot}1$.

292	175	106·3	2·02	346·5	195	91·6	2·00	406	210	82·6	2·03
,,	178	105·6	2·00	,,	228	91·4	2·00	,,	242	82·4	2·02
443	254	76·1	2·01	443	227	76·0	2·00				

Mean 2·01 ± 0·01.

n-*Propyl bromide* (b. p. 70·9°/761 mm.; $d_{4^\circ}^{20^\circ}$ 1·3538; Brühl, *Annalen*, 1880, **200**, 139, gives $d_{4^\circ}^{20^\circ}$ 1·3529); $P_E = 23{\cdot}7$.

348	98	106·3	2·14	380	150	101·1	2·17	413	160	94·2	2·15
,,	160	105·3	2·13	,,	136	100·4	2·16	,,	143	92·3	2·12
441	126	90·2	2·16	441	158	89·9	2·15				

Mean 2·15 ± 0·01.

iso*Propyl bromide* (b. p. 59·3°/757 mm.; $d_{4^\circ}^{20^\circ}$ 1·315; Brühl, *loc. cit.*, gives $d_{4^\circ}^{20^\circ}$ 1·310); $P_E = 24{\cdot}1$.

287	77	129·3	2·20	350	86	108·2	2·17	380	106	103·2	2·19
,,	85	128·7	2·19	,,	96	111·0	2·21	,,	89	101·5	2·17

Mean 2·19 ± 0·01.

n-*Butyl bromide* (b. p. 101·3°/758 mm.; $d_{4^\circ}^{20^\circ}$ 1·2745; I.C.T. give $d_{4^\circ}^{20^\circ}$ 1·275); $P_E = 28{\cdot}3$.

352	100	109·5	2·14	378	118	104·5	2·14	413	110	98·2	2·14
,,	95	109·5	2·14	,,	110	104·9	2·15	,,	138	98·0	2·14
445	110	95·1	2·17	474	161	89·7	2·15				
,,	146	95·1	2·17	,,	186	89·9	2·15				

Mean 2·15 ± 0·01.

sec.-*Butyl bromide* (b. p. 91°/754 mm.; $d_{4^\circ}^{25^\circ}$ 1·2508; Norris, Green, and Johnson, *Amer. Chem. J.*, 1901, **26**, 308, give $d_{4^\circ}^{25^\circ}$ 1·2507); $P_E = 28{\cdot}4$.

343	107	116·6	2·20	343	112	116·7	2·20

Mean 2·20.

When measurements were attempted at higher temperatures the substance decomposed rapidly.

tert-*Butyl bromide.* This decomposed at all temperatures at which measurements were attempted.

Methyl iodide (b. p. 42·6°/763 mm.; $d_{4^\circ}^{20^\circ}$ 2·278; interpolation from the data of Patterson, J., 1908, **93**, 1836, gives $d_{4^\circ}^{20^\circ}$ 2·2802); P_E = 1904.

T.	*p.*	*P.*	*μ.*	*T.*	*p.*	*P.*	*μ.*	*T.*	*p.*	*P.*	*μ.*
295	164	76·8	1·64	337	174	69·5	1·64				
,,	157	76·6	1·64	,,	157	69·5	1·64	Mean 1·64 ± 0·01.			

Ethyl iodide (b. p. 72·0°/758 mm.; $d_{4^\circ}^{20^\circ}$ 1·934; from data of Tyrer, J., 1914, **105**, 2534, $d_{4^\circ}^{20^\circ}$ = 1·9355); P_E = 24·3.

293	96	98·3	1·86	293	103	99·9	1·88	293	89	99·4	1·87
337	105	88·7	1·86	337	100	90·4	1·88	337	75	89·7	1·88

Mean 1·87 ± 0·01.

n-*Propyl iodide* (b. p. 102·4°/760 mm.; $d_{4^\circ}^{20^\circ}$ 1·7428; Brühl, *Annalen*, 1880, **203**, 15, gives $d_{4^\circ}^{20^\circ}$ 1·7427); P_E = 28·9.

337	97	104·7	2·01	337	97	104·4	2·01	337	74	104·6	2·01
374	127	97·4	2·01	374	100	97·6	2·02	374	126	97·7	2·02

Mean 2·01 ± 0·01.

n-*Butyl iodide* (b. p. 129·6°/760 mm.; $d_{4^\circ}^{20^\circ}$ 1·616; Brühl, *loc. cit.*, gives $d_{4^\circ}^{20^\circ}$ 1·6166); P_E = 33·5.

349	96	111·9	2·08	415	136	98·9	2·07	415	153	99·4	2·08
349	104	111·9	2·08	415	126	98·9	2·07	Mean 2·08 ± 0·01.			

Acetonitrile (b. p. 81·4°/758 mm.; $d_{4^\circ}^{20^\circ}$ 0·7822; I.C.T. give $d_{4^\circ}^{20^\circ}$ 0·7824); P_E = 11·1.

354	66	283·3	3·95	404	74	247·2	3·93	433	89	233·0	3·94
,,	68	280·7	3·93	,,	90	247·2	3·93	,,	77	232·2	3·93
463	96	218·2	3·94	463	103	217·9	3·93	Mean 3·94 ± 0·01.			

Propionitrile (b. p. 97·1°/759 mm.; $d_{4^\circ}^{20^\circ}$ 0·7822; I.C.T. give $d_{4^\circ}^{20^\circ}$ 0·7824); P_E = 15·8.

351	56	302·0	4·03	408	73	262·1	4·03	443	115	242·5	4·03
,,	67	302·6	4·03	,,	76	263·9	4·04	,,	67	241·0	4·01
469	56	231·8	4·05	469	132	230·6	4·03	Mean 4·03 ± 0·01.			

n-*Butyronitrile* (b. p. 116·6°/755 mm.; $d_{4^\circ}^{20^\circ}$ 0·7914; I.C.T. give $d_{4^\circ}^{20^\circ}$ 0·7909); P_E = 21·2.

339	57	321·4	4·06	375	68	289·5	4·04	407	82	269·0	4·04
,,	55	321·4	4·06	,,	70	289·8	4·04	,,	88	272·3	4·07
443	91	248·3	4·04	443	117	248·4	4·04	Mean 4·05 ± 0·01.			

Nitromethane. We are indebted to Dr. D. J. G. Ives for one specimen of this compound which had been purified for conductivity work. It had b. p. 99·1°/758 mm.; $d_{4^\circ}^{25^\circ}$ 1·1311. Wright, Murray-Rust, and Hartley (J., 1931, 199) give $d_{4^\circ}^{25^\circ}$ 1·1312. Since our results for this substance differed from those of Smyth and McAlpine (*loc. cit.*), another specimen was purified by us and had $d_{4^\circ}^{25^\circ}$ 1·1312. The measurements made with the second specimen are marked with an asterisk below. It will be seen that the two specimens gave almost identical moments. P_E = 12·5.

337	73	244·7	3·56	367	65	223·5	3·54	416	72	198·6	3·54*
,,	62	243·5	3·55	,,	89	227·1	3·57	,,	90	197·9	3·53*
416	93	200·9	3·56*	453	96	182·1	3·52*	454	108	183·7	3·54
453	100	182·6	3·53*	454	80	182·9	3·54	Mean 3·54 ± 0·01.			

Nitroethane (b. p. 113·1°/738 mm.; $d_{4^\circ}^{24\cdot3^\circ}$ 1·0469; $n_D^{24\cdot3^\circ}$ 1·3901; Brühl, *Z. physikal. Chem.*, 1895, **16**, 193, gives $d_{4^\circ}^{24\cdot3^\circ}$ 1·0472); P_E = 17·0.

365	65	232·5	3·56	389	82	220·9	3·58	428·0	107	201·9	3·57
,,	62	233·8	3·57	,,	90	220·6	3·57	,,	102	202·3	3·58
461	96	191·9	3·61	461	135	188·1	3·57	Mean 3·58 ± 0·01.			

α-*Nitropropane* [b. p. 131·4°/766 mm.; $d_{4^\circ}^{24\cdot3^\circ}$ 0·9974. This is lower than the value given by Brühl (*loc. cit.*), *viz.*, $d_{4^\circ}^{24\cdot3^\circ}$ 1·0081. Perkin (J., 1885, **46**, 688) gives $d_{25^\circ}^{25^\circ}$ 1·0023, whence $d_{4^\circ}^{25^\circ}$ 0·9994]; P_E = 21·4.

343	58	253·0	3·58	388	98	225·3	3·57	423	108	207·4	3·56
,,	60	252·6	3·58	,,	90	224·2	3·56	,,	117	207·2	3·56
466	107	193·0	3·59	466	143	189·8	3·56	Mean 3·57 ± 0·01.			

α-*Nitrobutane* (b. p. 151·8°/763 mm.; $d_{4^\circ}^{25^\circ}$ 0·9685; n_D 1·4078); P_E = 26·2.

373	79	238·4	3·57	416	72	214·0	3·55	441	88	204·5	3·56
,,	64	237·5	3·56	,,	97	213·3	3·54	,,	130	205·4	3·57
470	107	192·4	3·54	470	121	192·2	3·54	Mean 3·55 ± 0·01.			

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