134. *Studies in Dielectric Polarisation. Part XIII. The Dipole Moments of the Simpler Aliphatic Nitriles.*

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SEVERAL determinations of the dipole moments of the simpler aliphatic nitriles have previously been made, but the results obtained are somewhat widely divergent as is seen from Table I. (In all cases the solvent used was benzene.) From these data it is difficult to reach a decision on the important question as to whether the nitriles have a constant moment, which is independent of the length of the hydrocarbon chain, or whether the moment becomes larger with increasing length of the chain. On the whole, the latter view seems to be supported, although the individual values differ markedly. We have

TABLE I.

μ, in D units.

Temp.	25°.	20°.	18°.	20°.	25°.	(Vapour.)
Acetonitrile	3·4 [1]	3·11 [2]	3·51 [3]	3·16 [4]	3·45 [5]	3·94 [6]
Propionitrile	3·4 [1]	3·34 [2]	3·66 [3]	—	—	4·05 [6]
n-Butyronitrile	—	3·46 [2]	—	—	—	—

[1] Williams, *Z. physikal. Chem.*, 1928, **138**, 75.   [2] Werner, *ibid.*, 1929, B, **4**, 371.   [3] Eide and Hassel, *Tids. Kjemi*, 1930, **10**, 93.   [4] Hunter and Partington, J., 1932, 2812.   [5] Snoek, *Physikal. Z.*, 1934, **35**, 196.   [6] Højendahl, Thesis, Copenhagen, 1928 : values calculated from the data of Pohrt, *Ann. Physik*, 1913, **42**, 569.

therefore re-investigated the moments of pure specimens of four simple aliphatic nitriles and find that the dipole moment measured in benzene increases from aceto- to propionitrile, but then preserves a constant value in the higher members of the series, *viz.*, *n*-butyro- and *n*-valero-nitrile. The significance of this result is discussed on p. 608.

EXPERIMENTAL.

Dielectric Constants.—The electrical circuit, which is based on the heterodyne method, as previously used by us (J., 1933, 1252) and described by Hunter and Partington (J., 1932, 2812), has been improved in several respects. The two oscillators are contained in earthed copper boxes, and loosely coupled to the detector-amplifier; they are described in Part XII (preceding paper). The true capacities of the condensers are obtained correct to 0·02 $\mu\mu$F by translating the scale readings by means of large-scale calibration charts. The leads were as already described (*loc. cit.*). The sources of high and low tension are batteries of 120 volts, and three 2-volt accumulators, respectively, and these batteries are switched on about an hour before measurements are commenced. The zero point on the standard condenser is then quite steady, and the silent point is very sharp.

Dielectric Cell.—The dielectric cell consisted of a glass vessel, inside which the condenser plates of polished nickel were supported by nickel rods from the bakelite stopper, which was accurately ground to fit the glass vessel. Connexion to the standard condenser was made by a small bridge of stout copper wires, held rigidly apart, linking the small mercury cups on both the cell and the leads. The cell itself was immersed in a small, earthed, copper oil-bath, supported firmly on a ring of bakelite, which fitted a ground joint on the bottom of the glass container. The oil-bath was held in position in a large water thermostat, controlled at 20·0° $\pm$ 0·05°. The correction due to the leads was found by determining the capacity of the cell when filled with pure liquids of known dielectric constant. The electrical capacity of the cell was 52 $\mu\mu$F, and its volume 12 c.c.

Refractivities and Densities.—The refractivities were determined with a Pulfrich refractometer, and the densities by a 10-c.c. pyknometer. All measurements were made at 20·0° $\pm$ 0·05°. The refractive indices are correct to 0·0001, and the error on the densities is less than 0·0001.

Calculation of the Dipole Moment.—The symbols and method of calculation are the same as in previous parts of this series and, as before, the atomic polarisation is left undetermined. All electric moments are expressed in Debye units of 10^{-18} e.s.u.

Accuracy.—The dielectric constant of benzene is correct to $\pm$ 0·001 and those of solutions are correct to within 0·08%. The error on the polarisations of the solutes, $P_{2\infty}$, is not greater than 1·5 c.c., and the experimental errors on the electric moments are less than $\pm$ 0·02 D.

Preparation of Materials.—*Nitriles.* All the nitriles were purchased from Kahlbaum, with the exception of *n*-butyronitrile, which was supplied by Schuchardt. They were purified by standing over solid caustic potash for 2 days, to remove any acid formed by slight hydrolysis, then left in contact with calcium chloride for a week, to remove any ammonia, and finally dried by phosphoric oxide, over which they were twice fractionated. We have suggested (*Nature*, 1935, **135**, 474) that the previously recorded low values for acetonitrile may be, in part, due to the method of purification used, since repeated fractionation with phosphoric oxide would not remove traces of acetic acid, which has a dipole moment of about 0·8 D (Wolf, *Physikal. Z.*, 1930, **31**, 227). It is, however, very difficult to assess the purity of the materials used in previous work, since the observers have not recorded either the density or the refractive index of their specimens. The physical constants of the materials used in the present research are given in Table II.

TABLE II.

Compound.	B. p.	$D_{4°}^{20°}$.	$n_D^{20°}$.	$[R_L]$.
Acetonitrile	81·6°/760 mm.	0·7823	1·3438	11·12
Propionitrile	96·8/743	0·7830	1·3664	15·76
n-Butyronitrile	116·8/742	0·7911	1·3839	20·42
n-Valeronitrile	140·4/741	0·8014	1·3982	25·03

The following figures are available for comparison :

Acetonitrile : b.p. 81·7°/761·5 mm.; $D_D^{20°}$ 0·7825; $n_D^{20°}$ 1·3439 (Lowry and Henderson, *Proc: Roy. Soc.*, 1932, A, **136**, 471); $D_{4°}^{20°}$ 0·7823 (I.C.T.). Propionitrile : b. p. 97·0°/752·5 mm., $D_D^{20°}$ 0·7827, $n_D^{20°}$ 1·3661 (*idem, ibid.*); $D_{4°}^{20°}$ 0·783 (Walden, *Z. physikal. Chem.*, 1910, **70**, 575); b. p. 95·0°/722 mm. (Timmermans, *Proc. Roy. Dublin Soc.*, 1912, **13**, 310). *n*-Butyronitrile : b. p. 115·4°/739 mm. (*idem, ibid.*); $D_{4°}^{20°}$ 0·7909, $n_D^{20°}$ 1·383 (I.C.T.); $D_{4°}^{20°}$ 0·7904 (Hawkins, Clark, and Roberts, *J. Amer. Chem. Soc.*, 1920, **42**, 705). *n*-Valeronitrile : b. p. 141·7—142°/763 mm., $D_{4°}^{25°}$ 0·7949 (Kilpi, *Z. physikal. Chem.*, 1913, **86**, 671); $D_{4°}^{20°}$ 0·801, $n_D^{20°}$ 1·3909 (I.C.T.); $D_{4°}^{20°}$ 0·7935 (Morgan and Chazal, *J. Amer. Chem. Soc.*, 1913, **35**, 1821).

Benzene. The benzene used as solvent was Kahlbaum's " thiophen-free " material. It was dried over sodium and carefully fractionated. Kahlbaum's benzene " for analysis and molecular-weight determination " was subjected to the same treatment and used for calibrating the dielectric cell.

Results.—The solvent throughout is benzene, and all the measurements are at 20°.

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}, c.c.	P_2, c.c.
		Acetonitrile.					*Propionitrile.*		
0	2·280	0·8788	26·57	—	0	2·281	0·8789	26·58	—
0·00896	2·430	0·8782	28·58	250·6	0·00602	2·389	0·8784	28·08	275·8
0·01410	2·518	0·8780	29·68	247·0	0·00844	2·430	0·8782	28·63	269·5
0·01877	2·592	0·8777	30·56	239·4	0·01118	2·477	0·8781	29·24	264·5
0·02749	2·735	0·8774	32·18	230·6	0·01917	2·616	0·8775	30·97	255·6
0·03122	2·798	0·8773	32·86	227·9	0·02654	2·741	0·8770	32·44	247·4
0·03295	2·827	0·8770	33·17	226·9	0·03697	2·915	0·8764	34·33	236·2
0·04661	3·054	0·8763	35·41	216·2	0·04741	3·096	0·8756	36·16	228·6

$$P_{2\infty} = 262 \text{ c.c.}; \quad P_E = 11·1 \text{ c.c.};$$
$$P_{2\infty} - P_E = 250·9 \text{ c.c.}; \quad \mu = 3·44 \, D.$$

$$P_{2\infty} = 285 \text{ c.c.}; \quad P_E = 15·8 \text{ c.c.};$$
$$P_{2\infty} - P_E = 269·2 \text{ c.c.}; \quad \mu = 3·57 \, D.$$

f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_{4°}^{20°}$.	P_{12}, c.c.	P_2, c.c.
		n-Butyronitrile.					*n-Valeronitrile.*		
0	2·281	0·8789	26·58	—	0	2·281	0·8789	26·58	—
0·00757	2·417	0·8782	28·50	280·2	0·00670	2·400	0·8781	28·30	283·3
0·01131	2·486	0·8778	29·42	277·7	0·00958	2·452	0·8779	29·02	281·3
0·01651	2·578	0·8774	30·61	270·8	0·01362	2·522	0·8775	29·97	275·5
0·02183	2·675	0·8771	31·81	266·2	0·01881	2·611	0·8771	31·14	269·0
0·02729	2·770	0·8766	32·95	260·0	0·02654	2·746	0·8764	32·83	262·1
0·03653	2·935	0·8758	34·81	251·9	0·03924	2·969	0·8753	35·43	252·1
0·04562	3·101	0·8752	36·55	245·1	0·04630	3·095	0·8747	36·81	247·5

$$P_{2\infty} = 290 \text{ c.c.}; \quad P_E = 20·4 \text{ c.c.};$$
$$P_{2\infty} - P_E = 269·6 \text{ c.c.}; \quad \mu = 3·57 \, D.$$

$$P_{2\infty} = 295 \text{ c.c.}; \quad P_E = 25·0 \text{ c.c.};$$
$$P_{2\infty} - P_E = 270·0 \text{ c.c.}; \quad \mu = 3·57 \, D.$$

DISCUSSION OF RESULTS.

The following values of μ have been obtained :

Acetonitrile	3·44 D	*n*-Butyronitrile	3·57 D
Propionitrile	3·57 D	*n*-Valeronitrile	3·57 D

It has already been pointed out (*Nature*, 1935, **135**, 474) that the present value for acetonitrile is in excellent agreement with that of Snoek (*loc. cit.*), *viz.*, 3·45 D, as found from measurements in benzene, hexane, and carbon tetrachloride. It appears, however, that the existing values for propionitrile and *n*-butyronitrile are incorrect (see Table I). The moment of *n*-valeronitrile has been determined for the first time. The indications of the present results are given on p. 608.

With the exception of Williams's values (*loc. cit.*), which are probably to be regarded as superseded, all the previous determinations in solution, although they exhibit differences amongst themselves, agree in making the moment of propionitrile higher than that of acetonitrile. This is supported by the approximate values for the vapours calculated by Højendahl (*loc. cit.*). Werner (*loc. cit.*) detected a regular variation of dielectric

constant, moment, and molar volume through the series of nitriles. In general, there is no direct relationship between the dielectric constant of a substance and its moment, and the present values show that in the case of the cyanides, there is no proportionality between the molar volume and the moment.

The moments found for these nitriles may now be compared with those for other similar series of compounds. The simplest of these is that comprising the alkyl halides, for which accurate values of the moments are available. It is well established that there is a definite increase in moment from the hydrogen halide extending as far as the ethyl compound : this is illustrated in Table III. It is quite generally found that the moment

TABLE III.

	Fluoride.	Chloride.	Bromide.	Iodide.	Cyanide. Solution.	Cyanide. Vapour.
Hydrogen	—	1·02 [2]	0·78 [2]	0·38 [2]	2·65 [4]	2·93 [6]
Methyl	1·81 [1]	1·86 [3]	1·78 [1]	1·59 [1]	3·44 [5]	3·94 [7]
Ethyl	1·92 [1]	2·04 [3]	2·02 [1]	1·90 [1]	3·57 [5]	4·05 [7]
n-Propyl	—	2·04 [3]	—	—	3·57 [5]	—
n-Butyl	—	2·04 [1]	—	—	3·57 [5]	—

[1] Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499.   [2] Zahn, *Physical Rev.*, 1926, **27**, 455. [3] Sänger, *Physikal. Z.*, 1931, **32**, 20; cf. Fuchs, *Z. Physik*, 1930, **63**, 824.   [4] Werner, *loc. cit.* [5] Present research.   [6] Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697.   [7] Højendahl, *loc. cit.*

of a substance is higher in the vapour state than in solution. Hydrogen cyanide in the vapour state has a moment of 2·93 *D*, which is higher than the values found in solution by Werner (*loc. cit.*), 2·65 *D*, and by Lutgert (*Z. physikal. Chem.*, 1931, *B*, **14**, 27), 2·53 *D*. Smyth ("Dielectric Constant and Molecular Structure," 1931, 74) assumes that the principal dipole of the halides induces moments along the hydrocarbon chain, resulting in an increase of moment in the homologous series. The figures in Table III indicate, however, that this increase is detectable only as far as the ethyl compound.

Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367), from considerations based on wave mechanics and a probable electronic structure of the molecule, concludes that the hydrogen cyanide molecule is linear, and a photographic investigation of the band spectra of the vapour in the near infra-red region (Badger and Binder, *Physical Rev.*, 1931, **37**, 800) confirms this result. Choi and Barker (*ibid.*, 1932, **42**, 777) and Brackett and Liddel (*Smith. Misc. Collect.*, 1931, **85**, No. 5) have also concluded, from the infra-red absorption spectrum of the acid, that the molecule is linear, and this configuration may be regarded as well established.

A consideration of the dipole moments of the aromatic nitriles also throws some light on this matter. If the C–CN group is straight, it would be expected that vector-addition rules would apply to *p*-substituted benzene compounds containing only groups the moments of which act in the direction of the carbon valencies of the benzene ring. The results for some of these compounds (cf. Hampson and Sutton, *Proc. Roy. Soc.*, 1933, *A*, **140**, 562) are given below :

Compound.	μ, obs.	μ, calc.	Compound.	μ, obs.	μ, calc.
p-Toluonitrile	4·37	4·35	*p*-Bromobenzonitrile	2·64	2·38
p-Nitrobenzonitrile	0·69	0·03	*p*-Iodobenzonitrile	2·80	2·63
p-Chlorobenzonitrile	2·61	2·34			

The values (in *D*) are calculated from the following moments : $Ph \cdot NO_2$ 3·93, $Ph \cdot CN$ 3·90, $PhCl$ 1·56, $PhBr$ 1·52, PhI 1·27, and $Ph \cdot CH_3$ 0·45.

The differences between the calculated and the observed values in this table have been accounted for in several ways. They may be due to the fact that the linking of the nitrile group to the ring makes an angle with the line joining the carbon and nitrogen atoms (Bergmann and Tschudnowsky, *Z. physikal. Chem.*, 1932, *B*, **17**, 116) ; or to inductive effects caused by the strongly polar nitro- or nitrile groups (Poltz, Heil, and Strasser, *ibid.*, p. 155) ; or to the neglect of the atomic polarisation (Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 1854). It is noteworthy that the observed and the calculated

values do not agree for *p*-substituted benzene compounds containing groups which are supposed to give rise to large opposed electromeric effects (Hampson and Sutton, *loc. cit.*), and this may explain the discrepancy. Since the differences are in most cases quite small, it may be assumed that the nitrile group has a linear structure in these aromatic compounds as well as in the aliphatic series.

The alkyl cyanides will then be comparable with the alkyl halides and hydrogen cyanide with hydrogen chloride. It might be expected that the dipole moments of the two classes of compound would be analogous, and that induction effects would occur in both series. It may be noted that the conclusion reached by Hunter and Partington (J., 1932, 2825), that the *iso*thiocyanate group has an extended structure, has been confirmed from a study of the Raman spectra of the compounds (Langseth, Nielsen, and Sorenson, *Z. physikal. Chem.*, 1934, *B*, **27**, 101). In this series, dipole induction effects occur. The large moment of hydrogen cyanide must be due to unequal sharing of the six electrons forming the three covalent links between the carbon and the nitrogen nuclei, $H\!:\!C\!:\!:\!N\!:$, the nitrogen atom being negative with respect to the carbon, since the moment of the nitrile group in aromatic compounds acts in the same sense as that of the nitro-group, *i.e.*, away from the ring (cf. Sidgwick, " The Covalent Link in Chemistry," 1933, 151).

The relative increase caused by induction in the nitriles is smaller than that in the case of the halides, in spite of the greater magnitude of the nitrile dipole. This is shown by the data in Table III. The increase from Smyth and McAlpine's value, 2·93 *D*, for hydrogen cyanide vapour, which is more accurate than earlier results, to the figure 3·94, calculated by Højendahl for acetonitrile vapour, is probably too large, since the latter value can only be regarded as approximate. It is evident that the induced moments in the nitriles are of the same order as in the chlorides, and that the induction extends as far as the ethyl compound in both series, although the dipole in the former is much larger. Smyth and McAlpine (*J. Chem. Physics*, 1934, **2**, 499) have shown that there are qualitative analogies and differences between the Raman frequencies and the dipole moments of the alkyl halides. The frequency, which probably corresponds to a longitudinal vibration in the carbon–halogen line, falls from the methyl to the ethyl compound and then remains constant as the hydrocarbon chain is lengthened. The decrease in frequency corresponds with an increase in moment. The figures for the *n*-chlorides and cyanides (Kohlrausch, " Der Smekal–Raman Effekt," 1931, 304) are given below :

Compound.	Raman frequency, $\Delta\nu$, cm.$^{-1}$		Compound.	Raman frequency, $\Delta\nu$, cm.$^{-1}$	
	Chloride.	Cyanide.		Chloride.	Cyanide.
Methyl	712	2250	*n*-Propyl	651	2245
Ethyl	655	2246	*n*-Butyl...............	650	2245 (*iso*-)

It will be seen that, in the nitrile series, the Raman frequency also falls from the methyl to the ethyl member and then becomes constant, although the change in this case is much smaller.

Smyth and Walls (*loc. cit.*) have attributed the larger difference between the moments of phenylacetonitrile and acetonitrile, as compared with that between the corresponding halides, to an inductive effect, but if we take the new value for acetonitrile, the differences are seen to be of the same order for all the compounds. This result supports the assumption that the inductive action of the nitrile group is no greater than that of halogens. It might be expected that the influence of the larger cyanide dipole would extend further along the chain, as is indicated by Werner's earlier results (*loc. cit.*), but when the locations of the dipoles are considered, it is evident that such an extension is improbable. Smyth and McAlpine (*J. Chem. Physics*, 1933, **1**, 190), on the assumption that the C–Cl dipole is located $\frac{7}{8}$ of the distance from the carbon to the chlorine nucleus (cf. Meyer, *Z. physikal. Chem.*, 1930, *B*, **8**, 190), have calculated moments for the halogenated methanes which are in good agreement with experimental values. The principal dipole in the hydrogen cyanide molecule is situated between the carbon and the nitrogen nucleus, although its exact position is unknown. Badger and Binder (*loc. cit.*) calculate the value $18\cdot79 \times 10^{-40}$ g. cm^2. for the moment of inertia of the hydrogen cyanide mole-

cule, and hence the C–N distance is found to be 1·15 Å.U. Mecke ("Structure of Molecules," ed. P. Debye, 1932, 30) gives the C–H distance as 1·08 Å.U. Meyer (*loc. cit.*) takes the C–Cl distance as 1·85 Å.U., and the C–C distance 1·55 Å.U. The position of the main dipole in methyl chloride is situated $\frac{7}{8} \times 1·76 = 1·54$ Å.U. from the carbon. The location of the principal dipole in hydrogen cyanide may be assumed, from a consideration of the centres of gravity of the charges, to be approximately mid-way between the carbon and the nitrogen nucleus. The distance of this dipole from the methyl carbon in aceto-nitrile is $\frac{1}{2} \times 1·15 + 1·55 = 2·13$ Å.U. Thus, although the magnitude of the principal dipole is greater in the nitriles than in the chlorides, the greater distance of the location of the dipole from the chain compensates for this, with the result that the induced moments are no larger in the first case than in the second.

SUMMARY.

The dipole moments of aceto-, propio-, *n*-butyro-, and *n*-valero-nitriles have been measured, and it has been shown that the moment increases in the series as far as propio-nitrile. Beyond this, the moments are constant. These results are discussed with reference to the alkyl halides and other nitriles.