254. *Studies in Dielectric Polarisation. Part XX. The Dependence of Polarisation and Apparent Moment of Nitriles upon Solvent and Temperature.*

By Eric G. Cowley and James R. Partington.

The influence of the solvent upon the dipole moment is of considerable interest and several theories of the effect have been proposed. In order to test the validity of the equations a large number of experimental figures is necessary. The present research has been undertaken to investigate two effects : (1) the influence of the dielectric constant of the solvent on the polarisation and on the apparent moment at a constant temperature, and (2) the influence of a change in temperature, and thus of the dielectric constant, with a particular solvent. These two factors were first studied by Müller (*Physikal. Z.*, 1933, **34**, 689; 1934, **35**, 346; *Trans. Faraday Soc.*, 1934, **30**, 729) and subsequently by others.

The present communication describes the measurements of the polarisations and apparent moments of propionitrile and benzonitrile in six solvents, *viz.*, hexane, *cyclo*hexane, carbon tetrachloride, benzene, toluene, and carbon disulphide, at various temperatures. The moments of these two nitriles have been previously determined in solution only in benzene. The earlier figures for propionitrile are given in a preceding paper in this series (Cowley and Partington, J., 1935, 604), and references to the determinations on benzonitrile are given in the " Table of Dipole Moments " (*Trans. Faraday Soc.*, 1934, **30**, Appendix, p. 60). The authors (*loc. cit.*) have already shown that the ethyl compound possesses the average moment, 3·57, of the simple aliphatic nitriles, the methyl compound alone being different. (Debye units are used here and throughout this paper.) The dipole moment of benzonitrile in benzene at 20° is found to be 4·02, slightly higher than the average of the values previously reported and also larger than the moment of nitrobenzene, 3·94 in benzene at 25° (Jenkins, J., 1934, 480). The former compound also possesses the higher moment in the vapour state, the values being 4·39 and 4·23 for benzonitrile and nitrobenzene respectively (Groves and Sugden, *ibid.*, p. 1094).

We have found that all the polarisation values measured in solution for propionitrile and benzonitrile are smaller than the vapour values for these compounds at the same temperature, and that the polarisation varies regularly with the dielectric constant of the solvent, being greatest in the solvent of lowest dielectric constant. The results are considered in the light of the solvent-effect equations in a later part of the paper.

The nitrobenzene and benzonitrile molecules are similar in several respects. The former compound has been the subject of extensive experiments (Müller, *Physikal. Z.*, 1933, **34**, 689; Jenkins, *loc. cit.*; *Trans. Faraday Soc.*, 1934, **30**, 739; Fairbrother, J., 1934, 1846; Govinda Rau and Narayanaswamy, *Proc. Indian Acad. Sci.*, 1935, *A*, **1**, 489), and the differences now found for the polarisations of benzonitrile in different solvents are of the same order as those found for nitrobenzene. The results of the present research are summarised in Table I, in which the temperature, t, the solvent, its dielectric constant, ε, and the polarisation at infinite dilution, $P_{2\infty}$, of the solute are given, together with the dipole moment, μ.

It has been shown that moments calculated from the slope of the P–$1/T$ line are frequently too small (Jenkins, *Trans. Faraday Soc.*, *loc. cit.*) owing to the change of the dielectric constant of the solvent with the temperature. We have therefore calculated the apparent moments at each temperature from the total polarisation at infinite dilution minus the electronic polarisation.

The figures in Table I show that the moment decreases with increase of dielectric constant of the solvent at any one temperature, and that, in a particular solvent, the moment falls as the temperature decreases. The graphs (Fig. 1) of the polarisation $P_{2\infty}$ against the dielectric constant of the solvent at 20° for the two compounds give curves of a similar shape and the variations are found to be regular within the limits of experimental error. The polarisation falls gradually from the value in hexane to that in benzene and then more rapidly to that in carbon disulphide. This is the case at other temperatures where several values have been determined. The differences between the variation of the polarisation of benzonitrile and of propionitrile with the dielectric constant of the solvent seem to be determined principally by the magnitude of the polarisation.

FIG. 1.

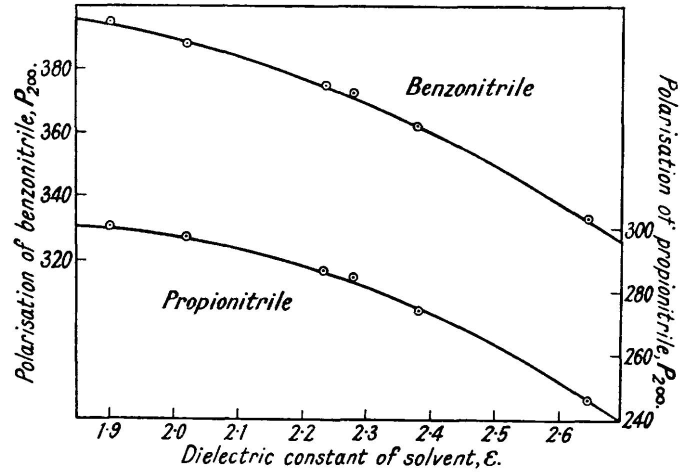


TABLE I.

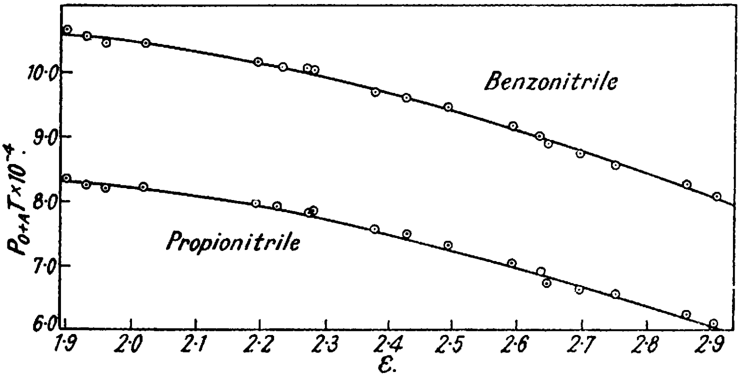
Solute.		Benzonitrile : P_E = 31·6 c.c.			Propionitrile : P_E = 15·8 c.c.		
Temp.	Solvent.	ε.	$P_{2\infty}$.	μ.	ε.	$P_{2\infty}$.	μ.
40°	CCl_4	2·195	356·0	4·05	2·195	270·0	3·58
20	C_6H_{14}	1·901	395·0	4·14	1·901	300·0	3·66
20	C_6H_{12}	2·020	388·0	4·10	2·020	297·0	3·65
20	CCl_4	2·234	375·0	4·03	2·234	287·0	3·58
20	C_6H_6	2·279	374·0	4·02	2·280	285·0	3·57 *
20	C_7H_8	2·379	362·0	3·95	2·379	272·0	3·48
20	CS_2	2·643	333·0	3·77	2·643	246·5	3·30
0	C_6H_{14}	1·929	418·0	4·12	1·931	317·0	3·64
0	CCl_4	2·275	400·0	4·03	2·275	304·0	3·56
0	C_7H_8	2·427	385·0	3·94	2·427	290·0	3·47
0	CS_2	2·694	351·0	3·75	2·691	259·5	3·28
−22·9	C_6H_{14}	1·964	447·0	4·09	1·965	340·0	3·62
−22·9	C_7H_8	2·489	410·0	3·91	2·489	308·0	3·43
−22·9	CS_2	2·753	374·0	3·72	2·750	278·0	3·25
−63·5	C_7H_8	2·590	468·0	3·84	2·590	353·0	3·38
−63·5	CS_2	2·862	425·0	3·64	2·859	315·0	3·18
−78·5	C_7H_8	2·632	494·0	3·81	2·632	373·0	3·35
−78·5	CS_2	2·906	446·0	3·61	2·903	330·0	3·15

* Cowley and Partington, J., 1935, 604.

The differences between the moments of benzonitrile and propionitrile under the same conditions from the measurements in Table I lie between 0·48 and 0·45 in all cases, *i.e.*, are practically constant. The difference for the vapours is given as 0·30 (Groves and Sugden, J., 1935, 971) and this is usually rather smaller than the difference in solution.

Müller (*Physikal. Z.*, 1934, **35**, 346) has shown, for solutions of nitrobenzene and methylene chloride in hexane and in carbon disulphide, that a smooth curve is obtained if the product P_0T (where P_0 is the orientation polarisation and T is the absolute temperature) is plotted against ϵ, the dielectric constant of the solvent. It was known that the electronic polarisation is practically independent of temperature as such, and Müller showed that it is uninfluenced by a change in solvent, so that, if the small effect of the atomic polarisation is neglected, the variation of P_0T is due to a change of the orientation polarisation with the dielectric constant of the solvent. The values of P_0T for the two nitriles are given in Table II with the dielectric constant of the solvent, ϵ, and the temperature of the measurement. The results are represented in Fig. 2. The curves resemble those obtained by Müller.

FIG. 2.



It is not possible to estimate the values of the atomic polarisation of the two compounds with any accuracy, since the value is uncertain owing to the change of moment with temperature, and is also particularly liable to be affected by error in determining the slope of the polarisation curve. The second error, which increases with the magnitude of the moment (because a small alteration in the slope of the P–$1/T$ line will markedly affect the intercept), will be important in these instances, as the moments are large. Extrapolation of the values found in the solvents where determinations were made at several temperatures gives values of the intercept of about 70 c.c. and 48 c.c. for benzonitrile and propionitrile, respectively. These correspond to the very high values of approximately 38 c.c. and 32 c.c.

TABLE II.

Solute.		Benzonitrile.			Propionitrile.		
Temp., abs.	Solvent.	ϵ of solvent.	P_{O+A},* c.c.	$P_0T \times 10^{-4}$.	ϵ of solvent.	P_{O+A},† c.c.	$P_0T \times 10^{-4}$.
293·0°	C_6H_{14}	1·901	363·4	10·65	1·901	284·2	8·33
273·0	C_6H_{14}	1·929	386·4	10·55	1·931	301·2	8·23
250·1	C_6H_{14}	1·964	415·4	10·39	1·965	324·2	8·11
273·0	C_6H_{12}	2·020	356·4	10·44	2·020	281·2	8·24
313·0	CCl_4	2·195	324·4	10·15	2·195	254·2	7·96
293·0	CCl_4	2·234	343·4	10·06	2·234	271·2	7·95
273·0	CCl_4	2·275	368·4	10·05	2·275	288·2	7·85
293·0	C_6H_6	2·279	342·4	10·03	2·280	269·2	7·89
293·0	C_7H_8	2·379	330·4	9·68	2·379	256·2	7·51
273·0	C_7H_8	2·427	353·4	9·64	2·427	274·2	7·49
250·1	C_7H_8	2·489	378·4	9·46	2·489	292·2	7·31
209·5	C_7H_8	2·590	436·4	9·14	2·590	337·2	7·06
194·5	C_7H_8	2·632	462·4	8·99	2·632	357·2	6·95
293·0	CS_2	2·643	298·4	8·83	2·643	230·7	6·76
273·0	CS_2	2·694	319·4	8·71	2·691	243·7	6·65
250·1	CS_2	2·753	342·4	8·56	2·750	262·2	6·56
209·5	CS_2	2·862	393·4	8·24	2·859	299·2	6·27
194·5	CS_2	2·906	414·4	8·06	2·903	317·2	6·17

* Obtained from $P_{2\infty}$ for benzonitrile (Table I) minus P_E (= 31·6 c.c.).

† Obtained from $P_{2\infty}$ for propionitrile (Table I) minus P_E (= 15·8 c.c.).

for the apparent atomic polarisation. High values of the atomic polarisation have been found by the temperature method, *e.g.*, for nitrobenzene in decalin P_A is 44 c.c. (Jenkins, *loc. cit.*) and in carbon tetrachloride 48 c.c. (Pal, *Phil. Mag.*, 1930, **10**, 267).

The dipole moments of propionitrile and benzonitrile in the vapour state are 4·05 (Höjendahl, Thesis, Copenhagen, 1928 : approximate value calculated from the data of Pohrt, *Ann. Physik*, 1913, **42**, 569) and 4·39 (Groves and Sugden, *loc. cit.*), respectively. These values are considerably higher than those found in solution, *e.g.*, 3·57 and 4·02 in benzene at 20° (present research), a result which might be expected for this type of molecule (cf. Frank, *Proc. Roy. Soc.*, 1935, *A*, **152**, 171). It is of some interest to see how far this difference can be accounted for by the various formulæ connecting the polarisations in the vapour state and in solution with the dielectric constant of the solvent.

Müller's empirical equation (*Physikal. Z.*, 1933, **34**, 689), *viz.*,

$$(P_2 - R)_{\text{solution}}/(P_2 - R)_{\text{vapour}} = 1 - \text{const.}(\varepsilon - 1)^2 \quad . \quad . \quad . \quad . \quad (1)$$

where const. = 0·075 ± 0·005, P_2 and R are the total polarisation and molecular refraction respectively, and ε is the dielectric constant of the solvent, represents very well the change of the polarisation in various solvents for a number of compounds, all having a radical on the dipole axis. The rule has been applied to the present results at 20° and the calculated values are given in Table III. For benzonitrile the values of the total polarisation and moment corrected to the vapour state, 420 c.c. and 4·28 respectively, may be compared with the values from the vapour measurements at 20°, *viz.*, 439 c.c. and 4·39 respectively. With the exception of that determined in carbon disulphide, the values are fairly consistent but are distinctly lower than the vapour value. A similar result has been noted for other compounds of large dipole moment, *e.g.*, the moment of nitromethane in heptane solution (3·17 at 25°) corrected to the vapour state gives 3·28, while the observed gas value is 3·42 (Smyth and McAlpine, *J. Amer. Chem. Soc.*, 1934, **56**, 1697 ; *J. Chem. Physics*, 1935, **3**, 557).

TABLE III.

Solute.	Benzonitrile.		Propionitrile.	
	Vapour values of $P_{2\infty}$ calc. from data in Table I by eqn. of			
Solvent.	Müller.	Sugden.	Müller.	Sugden.
C_6H_{14}	419	479	318	366
C_6H_{12}	431	478	331	368
CCl_4	419	476	322	366
C_6H_6	421	475	323	365
C_7H_8	417	466	315	353
CS_2	409	440	321	333
Mean of calc. values	420	469	322	358
Vapour value	439		347	

Another empirical relationship, proposed by Sugden (*Nature*, 1934, **133**, 415; *Trans. Faraday Soc.*, 1934, **30**, 720), is

$$P_{2\,\text{gas}} = P_{2\,\text{liq.}} - \alpha + P_O(\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $P_{2\,\text{liq.}}$ and $P_{2\,\text{gas}}$ are the total polarisation in solution in a solvent of dielectric constant ε and in the vapour state, respectively, P_O is the orientation polarisation in solution, and α is a small constant. The curve found by plotting the values of $P_{2\infty}$ for benzonitrile in various solvents at 20° against $(\varepsilon - 1)/(\varepsilon + 2)$ gives a value of $P_{2\infty}$ at $(\varepsilon - 1)/(\varepsilon + 2) = 0$ of 495 c.c., corresponding to a moment of 4·7, in agreement with the result of Sugden (*Nature, loc. cit.*) and considerably higher than the vapour value of 4·39 (*loc. cit.*). Table III contains the values of the vapour polarisations calculated by equation (2) from our results at 20°, α being neglected. In order to make the value of the polarisation calculated by (2) equal to the vapour value for benzonitrile, the constant α would have to be about 30 c.c. : it probably varies for one solute in different solvents (Jenkins and Sutton, J., 1935, 609).

In the place of these empirical rules, we may consider the theory of Raman and Krishnan

(*Proc. Roy. Soc.*, 1928, *A*, **117**, 589), which gives the relation between the polarisation and the dielectric constant for a pure substance in the liquid state by the expression

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4}{3}\pi\nu\left(\Sigma\frac{a_1}{3} + \frac{\mu^2}{3kT}\right) + \frac{\varepsilon - 1}{\varepsilon + 2}\nu\left(\Psi + \frac{\theta}{3kT}\right) \quad . \quad . \quad . \quad . \quad (3)$$

where ν is the number of molecules per c.c., a_1, a_2, a_3 are the moments induced in the molecule along the three axes by unit electric field, Ψ $[= \frac{1}{3}(a_1s_1 + a_2s_2 + a_3s_3)]$ and θ $(= \Sigma\mu_1{}^2s_1 + \Sigma 2\mu_1\mu_2q_{12})$ * involve the effect of anisotropy on the induced and orientation polarisations respectively, and the other symbols have their usual significance. The accuracy of this equation has been demonstrated by Krishnan (*ibid.*, 1929, *A*, **126**, 155) and others. Goss (J., 1933, 1341; 1934, 696) was the first to direct attention to the theory in connexion with the study of dipole moments and to the similarity between equations (2) and (3). The extension of (3) to liquid mixtures (Subbaramaiya, *Proc. Indian Acad. Sci.*, 1934, *A*, **1**, 355) leads to the expression

$$\frac{\varepsilon - 1}{\varepsilon + 2}\cdot\frac{M}{d_{12}} = f_1\cdot\frac{4}{3}\pi N\left(\Sigma\frac{a_1}{3} + \frac{\mu^2}{3kT}\right) + f_1\frac{\varepsilon - 1}{\varepsilon + 2}\cdot N\left(\Psi_1 + \frac{\theta_1}{3kT}\right)$$
$$+ f_2\frac{4}{3}\pi N\left(\Sigma\frac{a_1'}{3} + \frac{\mu'^2}{3kT}\right) + f_2\frac{\varepsilon - 1}{\varepsilon + 2}\cdot N\left(\Psi_2 + \frac{\theta_2}{3kT}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where f_1 and f_2 are the mol.-fractions of the two components, M, ε, and d_{12} are the " molecular weight," the dielectric constant, and density of the mixture, N is Avogadro's constant, and the anisotropic field constants contained in the functions Ψ_1, θ_1, Ψ_2, and θ_2 refer to the actual fields acting on the two types of molecules in the mixture.

Govinda Rau (*ibid.*, 1935, *A*, **1**, 498) reduces (4) in the case of a solution of a polar substance in a non-polar solvent ($\mu = 0$, $\theta_1 = 0$) to

$$P_2 = P_{2\infty} - N\Psi_1\frac{3\alpha\varepsilon_1}{(\varepsilon_1 + 2)^2} - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}N\Psi_2 - \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}\cdot\frac{N\theta}{3kT} \quad . \quad . \quad . \quad (5)$$

putting $\theta_2 = \theta$. P_2 is the polarisation value corrected for solvent influences, *i.e.*, the ideal gaseous value, $P_{2\infty}$ is the polarisation at infinite dilution in a solvent of dielectric constant ε_1, and α represents the change of dielectric constant with the concentration of the solution : $\varepsilon = \varepsilon_1(1 + \alpha f_2)$. The constants in Ψ_1 apply to the homogeneous solvent, but the constants in Ψ_2 and θ are those effective for the solute molecule in an infinitely dilute solution. Govinda Rau calculated, by the method of Raman and Krishnan (*loc. cit.*), the field constants in the last two expressions for an ellipsoidal cavity of the same shape as for benzene, and the moment is taken as the mean value in the various solvents. Although this treatment is only approximate, he found that his data and those of Narayanaswamy (*ibid.*, 1935, *A*, **1**, 489) corrected by equation (5) gave values for the nitrobenzene molecule which were close to the vapour value for this compound. The equation is general since it can explain the positive solvent effect (cf. also Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167).

With the same assumptions, the values calculated by equation (5) from our determinations are compared with the vapour value for benzonitrile in Table IV. The moment of benzonitrile is taken as 4·0.

TABLE IV.

Benzonitrile at 20°.

Solvent.	$P_{2\infty}$, c.c.	$-N\Psi_1\cdot\frac{3\alpha\epsilon_1}{(\epsilon_1 + 2)^2}$.	$-N\Psi_2\cdot\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$.	$\frac{-N\theta}{3kT}\cdot\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$.	P_2 gas, c.c.
C_6H_{14}	395	3·7	1·0	22·6	422
C_6H_{12}	388	3·2	1·1	25·3	418
CCl_4	375	0	1·2	28·4	405
C_6H_6....................	374	13·2	1·3	29·1	419
CS_2	330	0·7	2·4	31·7	368
				Vapour value	439

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* The q's denote the constants of the static polarisation field and the " s " terms are given by expressions of the type $q_{11} = \frac{4}{3}\pi + s_1$.

The constants given in Table V are taken from published data (Govinda Rau, *loc. cit.*; Krishnan and Rao, *Indian J. Physics*, 1929—30, **4**, 39; Ramanadham, *Proc. Indian Acad. Sci.*, 1934, *A*, **1**, 281).

The calculated values are somewhat smaller than the gas determination, that obtained from the anisotropic solvent carbon disulphide being considerably smaller. Since, however, the treatment is only approximate and the constants are uncertain, the agreement may be regarded as satisfactory. The average value of $P_{2\infty}$ from the first four solvents is 416 c.c., and the corresponding moment 4·26. The equation (5) gives at least as good agreement as the empirical equations.

Frank (*loc. cit.*) has developed a theory which accounts for the influence of solvent on the basis of molecular geometry. He plots the moment against the reciprocal of the dielectric constant of the solvent and obtains a straight line, which, when produced to the point $1/\varepsilon = 1$, gives a value slightly greater for certain compounds than the moment in the vapour state. The values in carbon disulphide and in polar solvents fall below the extension of the line found from other non-polar solvents. Since the moments determined in the usual solvents (hexane, $1/\varepsilon = 0{\cdot}53$, to carbon disulphide, $1/\varepsilon = 0{\cdot}38$) extend over a range of $1/\varepsilon$ of only 0·15 unit at 20°, it appears that the vapour moment can be obtained only approximately by such a method. The present values for the moment of benzonitrile, with the exception of the determination in carbon disulphide, can be fitted on a fairly good straight line with the vapour moment when plotted against $1/\varepsilon$.

TABLE V.

Solvent.	s_1.	s_2.	s_3.	$a_1 \times 10^{23}$.	$a_2 \times 10^{23}$.	$a_3 \times 10^{23}$.
C_6H_{14}	−1·78	0·89	0·89	1·44	1·67	1·07
C_6H_{12}	−0·75	−0·75	1·5	1·31	1·31	0·98
CCl_4	0	0	0	—	—	—
C_6H_6	−1·21	−1·21	2·42	1·41	1·41	0·71
CS_2	−0·91	0·46	0·46	1·43	0·59	0·59
Benzonitrile	—	—	—	1·74	1·74	0·87

Higasi (*Sci. Papers Inst. Phys. Chem. Res., Japan*, 1936, **28**, 284) represents the relation between solution and vapour moments by the equation

$$\mu_{\text{sol.}} = \mu + \Sigma\mu_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where μ_i is the sum of the induced moments produced by dissolving the substance in a solvent, and this latter term is evaluated for several types of molecule. He treats the solute molecule as an ellipsoid of rotation and has shown, for a molecule with a dipole along its axis of symmetry, and on the assumption that the radius *a* of the axis of symmetry is greater than that *c* perpendicular to it, that

$$\Sigma\mu_i = 4\pi\nu\alpha\mu A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where ν, α, and μ represent respectively the number of solvent molecules in unit volume, the polarisability of the solvent, and the moment of the solute vapour,

$$A = \frac{-1}{k^2 - 1}\left[1 - \frac{k}{\sqrt{k^2 - 1}}\log_e (k + \sqrt{k^2 - 1})\right] - \frac{1}{3} \quad . \quad . \quad . \quad . \quad (8)$$

and $a = kc$.

For this type of molecule, *A* is always negative ($k > 1$) and hence $\mu_{\text{sol.}}$ is smaller than μ [see equation (6)]. The value of *k* can be found from the Kerr constant, and thus *A* follows from (8). For the solvent the relation

$$\tfrac{4}{3}\pi\nu\alpha = (\varepsilon - 1)/(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

can be assumed, and thus $4\pi\nu\alpha$ is calculated. Higasi has estimated $\Sigma\mu_i/\mu$ and compared it with the observed value for a number of compounds. As the value of *k* is unknown for the two substances investigated in the present research, we have assumed the following values: for benzonitrile $k = 1{\cdot}69$ (*i.e.*, that of nitrobenzene; Higasi, *loc. cit.*), and for propionitrile $k = 1{\cdot}95$ [the mean of the values for HCN and C_4H_9CN (*ibid.*)]. The calculated and experimental values of $\Sigma\mu_i/\mu$ for the two nitriles are compared in Table VI (all results relating to 20°). The agreement is on the whole satisfactory, any divergencies for benzonitrile being of the same order as those found for nitrobenzene (Higasi, *loc. cit.*).

TABLE VI.

		Solute.					
		Benzonitrile (A = $-0·126$).			Propionitrile (A = $-0·154$).		
			$\Sigma\mu_i/\mu$.			$\Sigma\mu_i/\mu$.	
Solvent.	$4\pi\nu a$.	μ.	Exptl.	Calc.	μ.	Exptl.	Calc.
(Vapour)	—	4·39	—	—	4·05	—	—
C_6H_{14}	0·693	4·16	−0·05	−0·09	3·66	−0·10	−0·11
C_6H_{12}	0·761	4·10	−0·07	−0·10	3·65	−0·10	−0·12
CCl_4	0·873	4·03	−0·08	−0·11	3·58	−0·12	−0·13
C_6H_6...............	0·898	4·02	−0·08	−0·11	3·57	−0·12	−0·14
C_7H_8...............	0·945	3·95	−0·10	−0·12	3·48	−0·14	−0·15
CS_2	1·060	3·77	−0·14	−0·13	3·30	−0·18	−0·16

EXPERIMENTAL.

Electrical Apparatus.—The dielectric constants were determined by the apparatus previously used (Part XIII; J., 1935, 604).

FIG. 3.

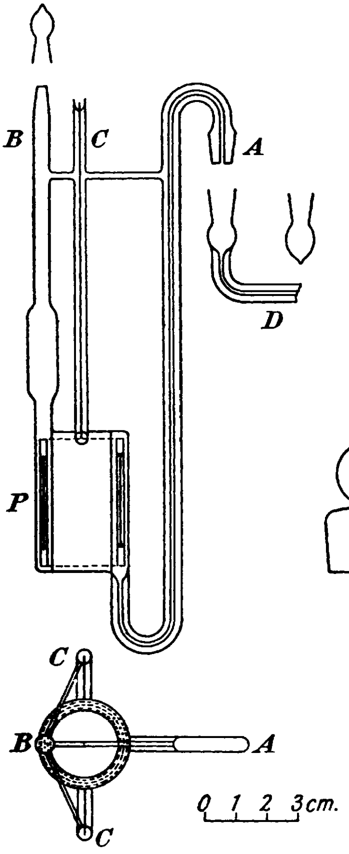
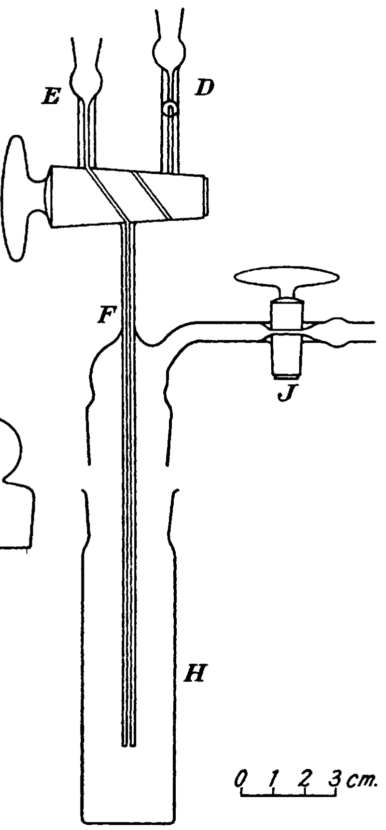


FIG. 4.



Dielectric Cell.—The dielectric cell (Fig. 3) consisted of an annular glass vessel inside which three concentric platinum cylinders (*P*) were fixed by small glass supports. The middle cylinder was insulated by small glass beads from the others, which were earthed. The platinum was 0·01 mm. in thickness, and the separation of the cylinders was 1 mm. Connexion to the cylinders was made by platinum wires, which were fused to the plates. These wires passed through glass tubes (*C*) to small mercury cups, which were linked by a small rigid bridge of copper wires to the mercury cups on the leads to the apparatus. The filling tubes (*A*, *B*) of the cell were closed by ground glass caps, and the ends of the four limbs were connected by glass rods which served to strengthen the cell. The cell was mounted on a heat-insulating cover so that the expansion bulb in the limb (*B*) was below it, and the weight of the cell was borne by a metal rod passing through the middle and a metal strip under the cell. A spring on the rod below the strip compensated for the differential expansion of the rod and the cell as the temperature varied. The cover and cell fitted a small, thin-walled, copper bath, which contained a small stirrer and thermocouple (see below). The bath was earthed and filled to a definite level with toluene, and the cell was always used in this bath. The electrical capacity of the cell, which was practically independent of temperature, was 56μμF and its volume 15 c.c.

The cell was filled by the apparatus shown in Fig. 4. The solutions were prepared in glass vessels (*H*) fitted with ground glass stoppers (*G*). The ground joints on the top of the vessels were interchangeable, so that all the vessels could fit a hollow stopper (*F*), through which a capillary passed. This capillary extended to the bottom of the vessel, and the other end passed to a two-way tap. The outlet tubes carried ground joints, one (*D*) fitting the ground joint (*A*) of the cell, and the other (*E*) that of the pyknometer. The solutions were blown into the cell, or pyknometer, by a stream of dry air through the tube (*J*), which carried a tap, and the flow of liquid was stopped by the tap (*T*) when the cell was full.

Densities.—The densities were determined by a pyknometer consisting of a long narrow bulb connected to the expansion bulb by a capillary tube. The ends of the capillaries were closed by ground caps. The pyknometer was aged by the method of Bretscher (*Physikal. Z.*, 1931, **32**, 768), and the coefficient of expansion determined by calibrating it with water at several temperatures.

Temperature Control.—A large Dewar vessel, contained in a heat-insulating box, served as a thermostat, and the small copper bath containing the cell was supported from the lid of this vessel. Above 0°, the temperature was maintained constant by circulating water through the vessel. Measurements at the lower temperatures were made at the f. p.'s of carbon tetrachloride and chloroform and at the sublimation point of solid carbon dioxide. For the first two, the temperature was kept constant by rapid stirring of solid and liquid, and for the last a paste of solid carbon dioxide and alcohol was used. The temperatures were taken as $-$ 22·9°, $-$ 63·5°, and $-$ 78·5° respectively (I.C.T., 1926, **1**, 53—54 : each value the mean of several determinations). The temperature was checked by small copper–constantan thermocouples, attached to a Tinsley potentiometer and sensitive moving-coil galvanometer. The thermocouples were constructed from 36 s.w.g. enamel-covered copper wire and 32 s.w.g. double silk-covered constantan wire (cf. Kraus and Vingee, *J. Amer. Chem. Soc.*, 1934, **56**, 511). The junctions, which were about ½ cm. long, were soldered by a cadmium–tin solder, covered with a layer of rosin. The four junctions were held in position on a wooden spacer, which fitted closely into a copper tube of outer diameter ½ cm. and wall-thickness ½ mm., the junctions being mounted as close to the walls as possible. The lower end of the tube was closed by soldering on a thin copper disc, and the other end was screwed into a bakelite cap. The wires outside the copper tube were protected by a rubber tube. One set of junctions was maintained at 0° throughout, and the sensitivity of the thermocouple at 20° was 0·0001590 volt per degree. Thermocouples were placed in the small cell-bath and in the main bath.

Preparation of Materials.—*Nitriles.* Propionitrile (Kahlbaum) was kept over caustic potash and then calcium chloride. It was dried by phosphoric oxide and twice fractionated. The properties of the two specimens used were : b. p. 96·8°/743 mm., $D_{4^\circ}^{20^\circ}$ 0·7830, $n_D^{20^\circ}$ 1·3664, $[R_L]_D$ 15·76 c.c.; b. p. 96·0°/730 mm., $D_{4^\circ}^{20^\circ}$ 0·7829, $n_D^{20^\circ}$ 1·3663, $[R_L]_D$ 15·76 c.c. Figures for comparison are : b. p. 97·0°/752·5 mm., $D_{4^\circ}^{20^\circ}$ 0·7827, $n_D^{20^\circ}$ 1·3661 (Lowry and Henderson, *Proc. Roy. Soc.*, 1932, *A*, **136**, 471).

Benzonitrile was steam distilled, extracted with ether, and fractionated in a vacuum. It was then left over phosphoric oxide for a day, fractionated under reduced pressure, and refractionated. The properties were : b. p. 190·8°/763 mm., $D_{4^\circ}^{20^\circ}$ 1·0046, $n_D^{20^\circ}$ 1·5289, $[R_L]_D$ 31·62 c.c. Previous determinations are : b. p. 190·6°/760 mm. (Kahlbaum and Wirkner, *Z. physikal. Chem.*, 1898, **26**, 603); 190·7° corr. (Perkin, J., 1896, **69**, 1249); 190·6° corr. (Wuyts, *Bull. Soc. chim.*, 1909, **5**, 409); $n_D^{20^\circ}$ 1·5289 (Berliner, Diss., Breslau, 1886); $D_{20^\circ}^{20^\circ}$ 1·0066 (Perkin, J., 1896, **69**, 1206); $D_{4^\circ}^{20^\circ}$ 1·0051 (Turner and Merry, *ibid.*, 1910, **97**, 2075).

Solvents. Hexane (Hopkin and Williams) was shaken with slightly diluted sulphuric acid several times, washed with water, and shaken with dilute alkaline potassium permanganate solution. After further washing, it was dried by calcium chloride and finally fractionated over sodium.

*cyclo*Hexane (Hopkin and Williams) was shaken over fuming sulphuric acid, and washed successively with water, caustic soda solution, dilute permanganate solution, and water. It was dried by calcium chloride and potassium carbonate, and twice fractionated.

Carbon tetrachloride (Kahlbaum " for analysis ") was dried over caustic potash and fractionated.

Benzene and toluene (both Kahlbaum's " for analysis ") were dried over sodium wire and fractionated. Carbon disulphide (Kahlbaum " for analysis ") was shaken with mercury but no blackening occurred. The liquid was dried and fractionated over phosphoric oxide.

Results.—The symbols and method of calculation are those previously used in this series. The moments are calculated at each temperature from $P_{2\infty}$ minus P_{E}, P_{A} being included in the orientation polarisation. The solvent and temperature of each measurement are stated.

Solute : Benzonitrile.

In hexane at 20°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·901	0·6731	29·58	—
0·005142	1·976	0·6747	31·37	377·7
0·008818	2·028	0·6761	32·57	368·7
0·015089	2·117	0·6781	34·57	360·3
0·020388	2·192	0·6800	36·16	352·3

$P_{2\infty}$ = 395·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 363·4 c.c.; μ = 4·14.

In hexane at −22·9°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·964	0·7108	29·47	—
0·005142	2·055	0·7121	31·50	425·2
0·008818	2·188	0·7130	32·85	412·8
0·015089	2·227	0·7146	35·09	401·9
0·020388	2·318	0·7160	36·87	392·3

$P_{2\infty}$ = 447·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 415·4 c.c.; μ = 4·09.

In carbon tetrachloride at 40°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·195	1·5558	28·17	—
0·004608	2·283	1·5528	29·62	342·9
0·009786	2·379	1·5497	31·16	333·7
0·013779	2·455	1·5472	32·33	330·1
0·018084	2·537	1·5446	33·54	325·1

$P_{2\infty}$ = 356·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 324·4 c.c.; μ = 4·05.

In carbon tetrachloride at 0°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·275	1·6325	28·10	—
0·004608	2·382	1·6295	29·73	381·8
0·009786	2·502	1·6263	31·46	371·4
0·013779	2·596	1·6238	32·75	365·6
0·018084	2·697	1·6213	34·08	358·8

$P_{2\infty}$ = 400·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 368·4 c.c.; μ = 4·03.

In toluene at 20°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·379	0·8663	33·48	—
0·005042	2·474	0·8670	35·02	338·9
0·009974	2·565	0·8676	36·44	330·2
0·014973	2·662	0·8683	37·88	327·3
0·019845	2·755	0·8689	39·21	322·2

$P_{2\infty}$ = 362·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 330·4 c.c.; μ = 3·95.

In toluene at −22·9°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·489	0·9056	33·74	—
0·005042	2·607	0·9063	35·47	376·9
0·009974	2·719	0·9069	37·04	364·6
0·014973	2·838	0·9075	38·62	359·7
0·019845	2·955	0·9082	40·10	354·2

$P_{2\infty}$ = 410·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 378·4 c.c.; μ = 3·91.

In toluene at −78·5°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·632	0·9566	33·91	—
0·005402	2·799	0·9572	36·09	466·3
0·009974	2·960	0·9577	38·05	449·0
0·014973	3·126	0·9583	39·93	436·0
0·019845	3·289	0·9589	41·66	423·0

$P_{2\infty}$ = 494·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 462·4 c.c.; μ = 3·81.

In carbon disulphide at 0°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·694	1·2902	21·29	—
0·004392	2·859	1·2879	22·65	331·0
0·008752	3·019	1·2859	23·89	318·4
0·012323	3·153	1·2840	24·87	312·6
0·017857	3·352	1·2813	26·27	300·2

$P_{2\infty}$ = 351·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 319·4 c.c.; μ = 3·75.

In carbon disulphide at −63·5°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·862	1·3800	21·12	—
0·004392	3·094	1·3772	22·76	394·5
0·008752	3·313	1·3743	24·19	371·9
0·012323	3·490	1·3727	25·26	357·1
0·017857	3·740	1·3694	26·79	338·7

$P_{2\infty}$ = 425·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 393·4 c.c.; μ = 3·64.

In hexane at 0°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·929	0·6894	29·54	—
0·005142	2·011	0·6904	31·46	403·0
0·008818	2·068	0·6919	32·74	392·3
0·015089	2·166	0·6937	34·86	382·1
0·020388	2·249	0·6952	36·57	374·8

$P_{2\infty}$ = 418·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 386·4 c.c.; μ = 4·12.

In *cyclo*hexane at 20°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·020	0·7781	27·43	—
0·006893	2·140	0·7795	29·76	365·5
0·013849	2·258	0·7809	31·93	352·4
0·021593	2·393	0·7825	34·26	343·7
0·027872	2·501	0·7837	36·02	335·6

$P_{2\infty}$ = 388·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 356·4 c.c.; μ = 4·10.

In carbon tetrachloride at 20°.

f_2.	ε.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·234	1·5941	28·13	—
0·004608	2·332	1·5913	29·68	364·5
0·009786	2·441	1·5883	31·33	355·1
0·013779	2·526	1·5858	32·56	349·6
0·018084	2·617	1·5831	33·83	342·6

$P_{2\infty}$ = 375·0 c.c.; P_{E} = 31·6 c.c.;
$P_{2\infty} - P_{\text{E}}$ = 343·4 c.c.; μ = 4·03.

In benzene at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·279	0·8786	26·56	—
0·006139	2·420	0·8794	28·58	355·6
0·014029	2·602	0·8806	31·00	342·6
0·023082	2·809	0·8817	33·56	329·8
0·031910	3·019	0·8828	35·93	320·2

$P_{2\infty}$ = 374·0 c.c.; P_E = 31·6 c.c.;

$P_{2\infty}$ − P_E = 342·4 c.c.; μ = 4·02.

In toluene at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·427	0·8846	33·56	—
0·005042	2·533	0·8853	35·20	358·8
0·009974	2·635	0·8861	36·71	349·4
0·014973	2·742	0·8868	38·22	344·8
0·019845	2·845	0·8875	39·61	338·4

$P_{2\infty}$ = 385·0 c.c.; P_E = 31·6 c.c.;

$P_{2\infty}$ − P_E = 353·4 c.c.; μ = 3·94.

In toluene at −63·5°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·590	0·9426	33·85	—
0·005042	2·737	0·9432	35·83	426·6
0·009974	2·874	0·9439	37·56	405·8
0·014973	3·015	0·9445	39·25	394·5
0·019845	3·154	0·9451	40·82	385·1

$P_{2\infty}$ = 468·0 c.c.; P_E = 31·6 c.c.;

$P_{2\infty}$ − P_E = 436·4 c.c.; μ = 3·84.

In carbon disulphide at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·643	1·2633	21·32	—
0·004392	2·791	1·2613	22·60	312·7
0·008752	2·937	1·2589	23·79	303·5
0·012323	3·057	1·2573	24·74	298·8
0·017857	3·241	1·2546	26·11	289·5

$P_{2\infty}$ = 330·0 c.c.; P_E = 31·6 c.c.;

$P_{2\infty}$ − P_E = 298·4 c.c.; μ = 3·77.

In carbon disulphide at −22·9°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·753	1·3237	21·21	—
0·004392	2·941	1·3218	22·66	351·4
0·008752	3·124	1·3198	23·98	337·7
0·012323	3·274	1·3180	25·01	329·6
0·017857	3·503	1·3154	26·49	316·9

$P_{2\infty}$ = 374·0 c.c.; P_E = 31·6 c.c.;

$P_{2\infty}$ − P_E = 342·4 c.c.; μ = 3·72.

In carbon disulphide at −78·5°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·906	1·4047	21·05	—
0·004392	3·166	1·4019	21·80	419·5
0·008752	3·416	1·3986	24·35	398·1
0·012323	3·615	1·3966	25·49	381·4

$P_{2\infty}$ = 446·0 c.c.; P_E = 31·6 c.c.;

$P_{2\infty}$ − P_E = 414·4 c.c.; μ = 3·61.

Solute : *Propionitrile.*

In hexane at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·901	0·6730	29·56	—
0·005217	1·956	0·6733	30·86	278·8
0·010577	2·009	0·6735	32·07	266·8
0·015341	2·056	0·6738	33·10	260·3
0·021246	2·117	0·6741	34·41	257·8

$P_{2\infty}$ = 300·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 284·2 c.c.; μ = 3·66.

In hexane at −22·9°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·965	0·7107	29·50	—
0·005276	2·034	0·7111	30·99	311·9
0·010999	2·102	0·7116	32·39	292·2
0·016030	2·159	0·7120	33·52	280·3
0·022380	2·232	0·7125	34·91	271·3

$P_{2\infty}$ = 340·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ = P_E − 324·2 c.c.; μ = 3·62.

In hexane at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	1·931	0·6898	29·58	—
0·005276	1·993	0·6902	30·98	294·9
0·010999	2·055	0·6906	32·32	278·7
0·016030	2·108	0·6910	33·43	269·8
0·022380	2·178	0·6914	34·84	264·6

$P_{2\infty}$ = 317·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 301·2 c.c.; μ = 3·64.

In *cyclo*hexane at 20°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·020	0·7781	27·43	—
0·005127	2·089	0·7780	28·71	277·7
0·010517	2·154	0·7780	29·93	265·1
0·015993	2·220	0·7780	31·09	256·3
0·019049	2·255	0·7780	31·68	250·5

$P_{2\infty}$ = 297·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 281·2 c.c.; μ = 3·65.

In carbon tetrachloride at 40°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·195	1·5558	28·17	—
0·005996	2·280	1·5518	29·53	255·0
0·012295	2·367	1·5481	30·85	246·1
0·018221	2·448	1·5446	32·04	241·6
0·022652	2·510	1·5421	32·91	237·4

$P_{2\infty}$ = 270·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 254·2 c.c.; μ = 3·58.

In carbon tetrachloride at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·275	1·6325	28·10	—
0·005996	2·380	1·6288	29·65	286·6
0·012295	2·488	1·6252	31·14	275·3
0·018221	2·589	1·6219	32·45	266·8
0·022652	2·661	1·6191	33·36	260·0

$P_{2\infty}$ = 304·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 288·2 c.c.; μ = 3·56.

In toluene at 0°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·427	0·8846	33·56	—
0·006104	2·525	0·8844	35·01	271·1
0·012239	2·618	0·8841	36·32	259·1
0·018399	2·714	0·8837	37·62	254·2
0·023759	2·798	0·8835	38·69	249·5

$P_{2\infty}$ = 290·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 274·2 c.c.; μ = 3·47.

In toluene at −63·5°.

f_2.	ε.	$D^{t^\circ}_{4^\circ}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·590	0·9426	33·85	—
0·006104	2·725	0·9422	35·60	320·6
0·012239	2·854	0·9417	37·17	305·1
0·018399	2·989	0·9414	38·71	298·0
0·023759	3·101	0·9411	39·92	289·3

$P_{2\infty}$ = 353·0 c.c.; P_E = 15·8 c.c.;

$P_{2\infty}$ − P_E = 337·2 c.c.; μ = 3·38.

In carbon disulphide at 20°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·643	1·2632	21·32	—
0·004604	2·761	1·2605	22·31	236·3
0·009270	2·879	1·2577	23·25	229·5
0·014066	2·996	1·2546	24·15	222·5
0·017974	3·092	1·2522	24·85	217·7

$P_{2\infty}$ = 246·5 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 230·7 c.c.; μ = 3·30.

In carbon disulphide at −22·9°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·750	1·3221	21·20	—
0·004604	2·895	1·3202	22·29	257·9
0·009270	3·032	1·3169	23·28	245·6
0·014060	3·171	1·3140	24·23	236·6
0·017974	3·281	1·3090	24·95	231·5

$P_{2\infty}$ = 278·0 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 262·2 c.c.; μ = 3·25.

In carbon tetrachloride at 20°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·234	1·5941	28·13	—
0·005996	2·330	1·5907	29·59	271·7
0·012295	2·428	1·5872	31·01	262·4
0·018221	2·519	1·5834	32·27	255·3
0·022652	2·586	1·5809	33·16	250·2

$P_{2\infty}$ = 287·0 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 271·2 c.c.; μ = 3·58.

In toluene at 20°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·379	0·8663	33·48	—
0·006104	2·467	0·8660	34·84	256·3
0·012239	2·554	0·8657	36·12	249·2
0·018399	2·642	0·8655	37·36	244·4
0·023759	2·717	0·8653	38·38	239·7

$P_{2\infty}$ = 272·0 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 256·2 c.c.; μ = 3·48.

In toluene at −22·9°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·489	0·9055	33·74	—
0·006104	2·596	0·9052	35·25	281·1
0·012239	2·701	0·9048	36·65	271·5
0·018399	2·806	0·9045	37·98	264·2
0·023759	2·904	0·9043	39·16	261·9

$P_{2\infty}$ = 308·0 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 292·2 c.c.; μ = 3·43.

In toluene at −78·5°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·632	0·9566	33·91	—
0·006104	2·784	0·9562	35·83	348·5
0·012239	2·929	0·9557	37·53	329·7
0·018399	3·078	0·9554	39·16	319·3
0·023759	3·205	0·9550	40·46	309·6

$P_{2\infty}$ = 373·0 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 357·2 c.c.; μ = 3·35.

In carbon disulphide at 0°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·691	1·2911	21·25	—
0·004604	2·820	1·2881	22·29	247·1
0·009270	2·947	1·2853	23·25	237·0
0·014066	3·077	1·2825	24·19	230·3
0·017974	3·178	1·2802	24·89	223·8

$P_{2\infty}$ = 259·5 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 243·7 c.c.; μ = 3·28.

In carbon disulphide at −63·5°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·859	1·3810	21·09	—
0·004604	3·030	1·3781	22·27	277·5
0·009270	3·191	1·3755	23·29	257·9
0·014066	3·348	1·3724	24·26	246·5
0·017974	3·480	1·3700	25·02	239·7

$P_{2\infty}$ = 315·0 c.c.; P_E = 15·8 c.c.;
$P_{2\infty} - P_E$ = 299·2 c.c.; μ = 3·18.

In carbon disulphide at −78·5°.

f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_{4°}^{t°}$.	P_{12}, c.c.	P_2, c.c.
0·000000	2·903	1·4045	21·04	—	0·007068	3·193	1·4002	22·91	285·6
0·004605	3·100	1·4017	22·33	301·2	0·010163	3·310	1·3987	23·61	273·9

$P_{2\infty}$ = 333·0 c.c.; P_E = 15·8 c.c.; $P_{2\infty} - P_E$ = 317·2 c.c.; μ = 3·15.

SUMMARY.

The polarisations and apparent moments of benzonitrile and propionitrile have been measured in six solvents at various temperatures. It has been shown that the apparent moment falls regularly as the dielectric constant of the solvent is increased at any one temperature, and that it also decreases in any solvent as the temperature is lowered. The data obtained from the solution measurements have been compared with the moments for the vapours by several formulæ, and it has been shown that the agreement between the observed and calculated values is fairly satisfactory, although in no case are the experimental data exactly reproduced.

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QUEEN MARY COLLEGE, UNIVERSITY OF LONDON. [*Received, May 30th,* 1936.]