457. *Molecular Polarisability. Anisotropic Polarisability of the Cyano-group from Molar Kerr Constants and Dipole Moments of Eight Nitriles*

By R. J. W. LE FÈVRE, B. J. ORR, and G. L. D. RITCHIE

Molar Kerr constants and apparent dipole moments are recorded at 25° for acetonitrile, propionitrile, isobutyronitrile, t-butyl cyanide, chloroacetonitrile, trichloroacetonitrile, and benzonitrile, all in carbon tetrachloride, and for malononitrile in benzene. Inductive effects in these molecules are briefly discussed. Estimates of the anisotropic polarisability of the C–CN group in various environments are obtained. A regular increase of anisotropy is apparent for the C–CN group in the series MeCN, $MeCH_2$·CN, Me_2CH·CN, Me_3C·CN. The C–CN data from MeCN are satisfactorily applicable to Cl_3C·CN, whilst, for $ClCH_2$·CN, those from Me_2CH·CN are most appropriate. The results for $CH_2(CN)_2$ are anomalous, suggesting either bending of the C–CN group, exaltation effects, or solute–solvent interactions. The C–CN group polarisability in C_6H_5·CN is much more anisotropic than in the aliphatic nitriles.

THE present measurements were initiated to extend, and test, existing information [1a] concerning the anisotropic polarisability of the C–CN group in nitriles. Previously recorded [2a] molar Kerr constants of acetonitrile and benzonitrile in carbon tetrachloride have been remeasured and complemented by measurements of the molar Kerr constants and dipole moments of propionitrile, isobutyronitrile, t-butyl cyanide, malononitrile, chloroacetonitrile, and trichloroacetonitrile. The results are summarised in Tables 1 and 2.

EXPERIMENTAL

Solutes.—Liquids were dried over phosphoric oxide (except for benzonitrile, for which magnesium sulphate was used) and redistilled at *ca.* 760 mm. immediately before making up solutions; collection temperatures were: acetonitrile, 81°; propionitrile, 96°; isobutyronitrile, 103°; chloroacetonitrile, 126°; benzonitrile, 190°. t-Butyl cyanide, fractionally crystallised, had m. p. 17°. Malononitrile, fractionally crystallised and redistilled at 123°/30 mm., had m. p. 30°. A commercial sample of trichloroacetonitrile was used without purification.

Solvents.—Carbon tetrachloride was employed as solvent, except for benzene in the case of malononitrile. Solvents were fractionated and dried prior to use.

Apparatus.—Dielectric constants were determined with apparatus as in ref. 3, associated procedures giving polarisations being standard.[1b] Kerr effects were recorded photometrically.[4]

Results.—These are listed in usual form in Tables 1 and 2. The symbols are those previously explained,[1b,2,3] and summarised.[5] For acetonitrile and benzonitrile, which have been examined already,[2a] only the Kerr effect has been remeasured.

Previous Measurements.—The dipole moments in Table 2 are in reasonable agreement with recorded values.[6] The only previously determined $_{\infty}({}_{m}K_2)$ values are for acetonitrile and benzonitrile, $+219{\cdot}5 \times 10^{-12}$ and $+1147 \times 10^{-12}$, respectively.[2a] The Kerr constants of acetonitrile, propionitrile, and benzonitrile were recently determined in the pure liquid state.[7] The

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[1] Le Fèvre, (*a*) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (*b*) " Dipole Moments," Methuen, London, 3rd edn., 1953, ch. 2.

[2] Le Fèvre and Le Fèvre, (*a*) *J.*, 1954, 1577; (*b*) *J.*, 1953, 4041; (*c*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*d*) Chapter XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, 3rd edn., Vol. I, p. 2459.

[3] Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

[4] Le Fèvre and Ritchie, *J.*, 1963, 4933.

[5] Le Fèvre and Sundaram, *J.*, 1962, 1494.

[6] Wesson, " Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948; McClellan, " Tables of Experimental Dipole Moments," Freeman, San Francisco, 1963; Mansingh, *Indian J. Pure Appl. Phys.*, 1964, **2**, 33.

[7] Hauser and Marshall, U.S. Dept. Com., Office Tech. Serv., P.B. Rept., 1961, **153**, 981.

values of R_D calculated by summation of the appropriate bond values of Vogel *et al.*[8] are (for comparison with the observed values in Table 2): propionitrile, 15·8 c.c.; isobutyronitrile, 20·4 c.c.; t-butyl cyanide, 25·1 c.c.; malononitrile, 15·6 c.c.; chloroacetonitrile, 16·0 c.c.; trichloroacetonitrile, 26·2 c.c.

TABLE 1

Incremental Kerr effects, dielectric constants, etc., for solutions at 25°*

Acetonitrile

10^5w_2	242	576	652	746	1242	1512
$10^{10}\Delta B$	128	306	367	428	715	847

whence $\Sigma\Delta B/\Sigma w_2 = 56\cdot1 \times 10^{-7}$.

Benzonitrile

10^5w_2	290	318	575	752	891	973
$10^{10}\Delta B$	310	342	619	802	956	1045

whence $\Sigma\Delta B/\Sigma w_2 = 107\cdot3 \times 10^{-7}$.

Propionitrile

10^5w_2	247	329	408	503	644	662
$10^4\Delta\varepsilon$	1079	1449	1777	2172	2754	2823
$-10^5\Delta d$	388	524	648	808	1030	1056
$-10^4\Delta n$	4	5	7	9	11	11
$10^{10}\Delta B$	112	151	184	226	286	292

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 43\cdot1$, $\Sigma\Delta d/\Sigma w_2 = -1\cdot59$, $\Sigma\Delta n/\Sigma w_2 = -0\cdot17$, $\Sigma\Delta n^2/\Sigma w_2 = -0\cdot49$, $\Sigma\Delta B/\Sigma w_2 = 44\cdot8 \times 10^{-7}$.

Isobutyronitrile

10^5w_2	349	427	501	630	682	720
$10^4\Delta\varepsilon$	1261	1541	1809	2269	2451	2579
$-10^5\Delta d$	583	715	838	1054	1134	1197
$-10^4\Delta n$	7	8	9	11	12	13
$10^{10}\Delta B$	126	156	186	229	246	262

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 36\cdot0$, $\Sigma\Delta d/\Sigma w_2 = -1\cdot67$, $\Sigma\Delta n/\Sigma w_2 = -0\cdot18$, $\Sigma\Delta n^2/\Sigma w_2 = -0\cdot53$, $\Sigma\Delta B/\Sigma w_2 = 36\cdot4 \times 10^{-7}$.

t-Butyl cyanide

10^5w_2	166	303	400	588	703	727
$10^4\Delta\varepsilon$	523	940	1214	1815	2163	2222
$-10^5\Delta d$	282	514	673	997	1193	1230
$-10^4\Delta n$	3	7	8	11	14	14
$10^{10}\Delta B$	48	87	116	174	209	215

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 30\cdot8$, $\Sigma\Delta d/\Sigma w_2 = -1\cdot69$, $\Sigma\Delta n/\Sigma w_2 = -0\cdot20$, $\Sigma\Delta n^2/\Sigma w_2 = -0\cdot58$, $\Sigma\Delta B/\Sigma w_2 = 29\cdot4 \times 10^{-7}$.

Malononitrile *

10^5w_2	312	493	670	799	966	1204
$10^4\Delta\varepsilon$	643	1018	1386	1640	1996	2468
$10^5\Delta d$	34	66	97	123	151	170
$-10^4\Delta n$	3	5	7	9	10	12
10^5w_2	312	493	670	799	801	966
	1032	1092	1204	1250		
$-10^{11}\Delta B$	50	141	152	181	199	226
	258	280	271	284		

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 20\cdot6$, $\Sigma\Delta d/\Sigma w_2 = 0\cdot14$, $\Sigma\Delta n/\Sigma w_2 = -0\cdot10$, $\Sigma\Delta n^2/\Sigma w_2 = -0\cdot31$, $\Sigma\Delta B/\Sigma w_2 = -2\cdot3_6 \times 10^{-7}$.

Chloroacetonitrile

10^5w_2	382	440	558	622	769	873
$10^4\Delta\varepsilon$	850	980	1236	1375	1698	1919
$-10^5\Delta d$	224	249	320	359	448	505
$-10^4\Delta n$	4	4	6	6	7	8
$10^{11}\Delta B$	297	336	420	479	587	672

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 22\cdot1$, $\Sigma\Delta d/\Sigma w_2 = -0\cdot58$, $\Sigma\Delta n/\Sigma w_2 = -0\cdot10$, $\Sigma\Delta n^2/\Sigma w_2 = -0\cdot28$, $\Sigma\Delta B/\Sigma w_2 = +7\cdot66 \times 10^{-7}$.

Trichloroacetonitrile

10^5w_2	2002	2921	3767	4889	5757	7163
$10^4\Delta\varepsilon$	1036	1512	1957	2538	2990	3737
$-10^5\Delta d$	388	529	668	798	978	1205
$-10^4\Delta n$	5	7	11	13	14	19
$10^{11}\Delta B$	272	353	477	625	732	877

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 5\cdot20$, $\Sigma\Delta d/\Sigma w_2 = -0\cdot17$ $\Sigma\Delta n/\Sigma w_2 = -0\cdot026$, $\Sigma\Delta n^2/\Sigma w_2 = -0\cdot076$, $\Sigma\Delta B/\Sigma w_2 = 1\cdot2_6 \times 10^{-7}$.

* All solutes were examined in carbon tetrachloride, except malononitrile, for which benzene was used.

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants

Solute	$\alpha\varepsilon_1$	β	$\gamma'n_1^2$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	γ	δ	10^{12} $_\infty(_mK_2)$
MeCN	55·7 †	−1·04 †	—	—	11·2 †	3·38 †	−0·18	801	+239
$MeCH_2\cdot CN$	43·1	−1·00	−0·49	271·8	16·0	3·53	−0·12	640	+256
$Me_2CH\cdot CN$	36·0	−1·05	−0·53	289·6	20·3	3·62	−0·12	520	+262
$Me_3C\cdot CN$	30·8	−1·07	−0·58	302·4	24·2	3·68	−0·14	420	+254
$CH_2(CN)_2$	20·6	0·165	−0·31	274·8	14·6	3·56	−0·07	−5·76	−72
$ClCH_2\cdot CN$	22·1	−0·365	−0·10	195·7	15·4	2·97	−0·07	109	+56·8
$Cl_3C\cdot CN$	5·20	−0·109	−0·076	108·9	26·3	1·99	−0·018	18·0	+18·0
$C_6H_5\cdot CN$	31·5 †	−0·560 †	—	—	31·6 †	4·02 †	0·08 †	1533	+1174

* It is assumed that $_DP = 1\cdot05R_D$. † From ref. 2*a*.

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[8] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

TABLE 3

Bond angles in various nitrile molecules

Molecule	$MeCH_2{\cdot}CN$	$Me_2CH{\cdot}CN$	$Me_3C{\cdot}CN$	$CH_2(CN)_2$	$ClCH_2{\cdot}CN$	$Cl_3C{\cdot}CN$
Angle	CCC	CCC	CCC	CCC	CCCl	CCCl
Assumed	110°	110°	109·5°	114°	112°	108·5° *
Lit. and ref.	110·5° [9]	—	109·5° [10]	113·7° [11]	111·5° [12]	109—110° [13]

* As in $MeC{\cdot}Cl_3$ (ref. 4).

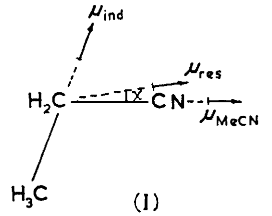
DISCUSSION

Molecular Geometry.—Bond angles used in the ensuing calculations are compared with literature values in Table 3. In all cases, the C–CN group has been assumed to be linear.

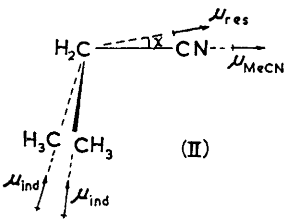
Magnitude and Direction of Dipole Moments.—For acetonitrile, t-butyl cyanide, malononitrile, trichloroacetonitrile, and benzonitrile, symmetry considerations allow unambiguous assignment of dipole-moment direction, but for the remaining molecules of the series it is necessary to make assumptions as to its direction.

For chloroacetonitrile, microwave studies [12a] indicate that the resultant dipole moment, μ_{res}, lies between the C–Cl and C–CN bond directions, at an angle of 28° ± 3° with the latter. Likewise, vectorial addition of the dipole moments [2a] of acetonitrile (3·38 D) and methyl chloride (1·72 D), separated by 112°, yields a resultant of 3·17 D, inclined at 30° to the C–CN axis. It is therefore assumed that μ_{res} of chloroacetonitrile (2·97 D, obs.) acts at 30° to the C–CN axis. It is of interest to note that the difference (—0·2 D) between the observed moment (2·97 D) and that calculated by addition of standard bond values (3·17 D) is of the same order as the corresponding differences for trichloroacetonitrile (—0·3 D) and malononitrile (—0·2 D), indicating similar apparent inductive effects in the three molecules.

The cases of propionitrile and isobutyronitrile may be treated in two ways: (a) inductive effects may be ignored, and μ_{res} assumed to lie along the C–CN axes, or (b) the observed dipole moment may be regarded as the resultant of the acetonitrile dipole moment (3·38 D), directed along the C–CN axis, and an induced moment, μ_{ind}, along each C–C bond adjacent to the C–CN group, as indicated by (I) and (II). Treatment (b) yields, for propionitrile, $\mu_{ind} = 0{\cdot}38$ D and $\chi = 5{\cdot}9°$, and, for isobutyrinitrile, 0·40 D and 6·4°. A similar treatment for t-butyl cyanide yields $\mu_{ind} = 0{\cdot}30$ D. It is perhaps significant that the moment apparently induced in a C–C bond adjacent to the C–CN group is of the same order in each of the three molecules considered. Treatments (a) and (b) probably represent opposite extremes of the true picture of the molecular dipole moment, and both will therefore be considered in the ensuing calculations.



(I)



(II)

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[9] Lerner and Dailey, *J. Chem. Phys.*, 1957, **26**, 678.

[10] Sparstad and Amble, *J. Chem. Phys.*, 1957, **27**, 317; Livingston and Rao, *J. Amer. Chem. Soc.*, 1959, **81**, 3584.

[11] Muller and Pritchard, *J. Amer. Chem. Soc.*, 1958, **80**, 3483; Hirota, *J. Mol. Spectroscopy*, 1961, **7**, 242.

[12] (*a*) Graybeal, *J. Chem. Phys.*, 1960, **32**, 1258; (*b*) Wada, Kikuchi, Matsumura, Hirota, and Morino, *Bull. Chem. Soc. Japan*, 1961, **34**, 337.

[13] Baker, Jenkins, Kenny, and Sugden, *Trans. Faraday Soc.*, 1957, **53**, 1397; Livingston, Page, and Rao, *J. Amer. Chem. Soc.*, 1960, **82**, 5048; Rajan, *Proc. Indian Acad. Sci.*, 1961, **53***A*, 89.

The values of χ for propionitrile and isobutyronitrile calculated by treatment (b) are of the same order as the corresponding angles (*ca.* 9 and 7°, respectively) estimated from the formal charge distribution data of Soundararajan.[14] Likewise, for chloroacetonitrile, Soundararajan's data indicate that μ_{res} is directed at 23·5° to the C–CN axis.

C–CN *Polarisabilities in* MeCN, $\text{Me}_3\text{C}\cdot\text{CN}$, *and* $\text{Cl}_3\text{C}\cdot\text{CN}$.—These molecules should, from their symmetry, have molecular polarisability ellipsoids of revolution (*i.e.*, specifiable by semi-axes b_1 and $b_2 = b_3$). Since the resultant dipole moments act in directions which correspond to b_1, the differences $(b_1 - b_2)$ can be computed from the ${}_{\infty}({}_{\text{m}}K_2)$'s and μ's of Table 2. The sums $(b_1 + 2b_2)$ are drawn from the related electronic polarisations, ${}_{\text{E}}P$. For acetonitrile, the refractivity data of Jeffery and Vogel[15] have been extrapolated[2a] to give ${}_{\text{E}}P = 10·85$ c.c. For t-butyl cyanide, summation of the appropriate bond values of Le Fèvre and Steel[16] gives ${}_{\text{E}}P = 24·53$ c.c. For trichloroacetonitrile, ${}_{\text{E}}P(\text{CCl}_3\cdot\text{CN}) = {}_{\text{E}}P(\text{CCl}_3\cdot\text{CH}_3) - {}_{\text{E}}P(\text{CH}_3) + {}_{\text{E}}P(\text{CN})$, where ${}_{\text{E}}P(\text{CCl}_3\cdot\text{CH}_3)$ has been estimated[4] from data of Vogel[17] as 25·58 c.c., and ${}_{\text{E}}P(\text{CH}_3)$ and ${}_{\text{E}}P(\text{CN})$ are derivable from Le Fèvre–Steel bond values. The above formula gives ${}_{\text{E}}P(\text{CCl}_3\cdot\text{CN}) = 25·36$ c.c. Molecular semi-axes then emerge as in Table 4. The values of b_1 and b_2 for acetonitrile in Table 4 are to be compared with $b_1 = 5·43$ and $b_2 = 3·70$, as in ref. 2*a*.

The values of b in Table 4, together with the usual polarisability values[1a] for C–C and C–H, the polarisabilities of the CCl_3 group extracted from 1,1,1-trichloroethane,[4] the ${}_{\text{E}}P$ of the C–CN group given by Le Fèvre and Steel,[16] and the bond angles already discussed, afford estimates (Table 5) of the longitudinal and transverse polarisabilities of the C–CN group ($b_{\text{L}}^{\text{CCN}}$ and $b_{\text{T}}^{\text{CCN}} = b_{\text{V}}^{\text{CCN}}$, respectively). For acetonitrile, the previously estimated values[1a] are $b_{\text{L}}^{\text{CCN}} = 3·7$ and $b_{\text{T}}^{\text{CCN}} = 1·8$. The close agreement between the CCN polarisabilities as extracted from acetonitrile and trichloroacetonitrile is to be noted. The increased anisotropy of the CCN group in t-butyl cyanide conforms to a trend already observed in the t-butyl halides,[1a] although the increase in anisotropy is considerably less in the present case.

TABLE 4

Calculation of semi-axes * for MeCN, $\text{Me}_3\text{C}\cdot\text{CN}$, and $\text{Cl}_3\text{C}\cdot\text{CN}$

	${}_{\text{E}}P$ (c.c.)	$(b_1 - b_2)$	$(b_1 + 2b_2)$	b_1	$b_2 = b_3$
MeCN	10·85	1·89	12·90	5·56	3·67
$\text{Me}_3\text{C}\cdot\text{CN}$	24·53	1·68	29·17	10·84	9·16
$\text{Cl}_3\text{C}\cdot\text{CN}$	25·36	0·41	30·16	10·33	9·92

* Here, and elsewhere, polarisabilities are quoted in cubic Angström units (10^{-24} c.c.).

TABLE 5

Values of b_{L} and b_{T} $(=b_{\text{V}})$ for the C–CN group in MeCN, $\text{Me}_3\text{C}\cdot\text{CN}$, and $\text{Cl}_3\text{C}\cdot\text{CN}$

	$b_{\text{L}}^{\text{CCN}}$	$b_{\text{T}}^{\text{CCN}}$	$(b_{\text{L}}^{\text{CCN}} + 2b_{\text{T}}^{\text{CCN}})$	$(b_{\text{L}}^{\text{CCN}} - b_{\text{T}}^{\text{CCN}})$
MeCN	3·64	1·75	7·14	1·89
$\text{Me}_3\text{C}\cdot\text{CN}$	4·03	1·54	7·11	2·49
$\text{Cl}_3\text{C}\cdot\text{CN}$	3·62	1·71	7·04	1·91

Polarisabilities of $\text{MeCH}_2\cdot\text{CN}$ *and* $\text{Me}_2\text{CH}\cdot\text{CN}$.—The symmetry of these molecules does not permit the derivation of unambiguous polarisability values. It is possible, however, to estimate the most appropriate bond-polarisabilities for the molecules, by comparing calculated values, ${}_{\text{m}}K$ (calc.), of the molar Kerr constant with the observed quantities, ${}_{\text{m}}K$ (obs.).

Adopting the geometry previously indicated, values of b_1, b_2, b_3 for both molecules

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[14] Soundararajan, *Indian J. Chem.*, 1963, **1**, 503.

[15] Jeffery and Vogel, *J.*, 1948, 675.

[16] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

[17] Vogel, *J.*, 1948, 1850.

TABLE 6

Evaluation of ${}_{\mathrm{m}}K$ (calc.) for $MeCH_2$·CN and Me_2CH·CN

Source of b^{CCN}	$b_{\mathrm{L}}^{\mathrm{CCN}}$, $b_{\mathrm{T}}^{\mathrm{CCN}}$ *	b_1, b_2, b_3 †	μ_1, μ_2, μ_3 ‡	$10^{12}{}_{\mathrm{m}}K$ (calc.)	$b_{\mathrm{L}}^{\mathrm{CCN}}$, $b_{\mathrm{T}}^{\mathrm{CCN}}$ *	b_1, b_2, b_3 †	μ_1, μ_2, μ_3 ‡	$10^{12}{}_{\mathrm{m}}K$ (calc.)
	$MeCH_2$·CN. *Treatment* (a), *with* μ_{res} *along* C–CN				$MeCH_2$·CN. *Treatment* (b), *with* μ_{ind} *along* C–Me			
MeCN	3·64	7·24	+3·482		3·64	7·24	+3·403	
	1·75	5·81	+0·579	+231	1·75	5·81	+0·931	+218
	1·75	5·22	0		1·75	5·22	0	
Me_3C·CN	4·03	7·62	+3·506		4·03	7·62	+3·444	
	1·54	5·61	+0·410	+315	1·54	5·61	+0·766	+301
	1·54	5·01	0		1·54	5·01	0	
Interpolated	3·75	7·34	+3·493		3·82	7·41	+3·428	
	1·67	5·74	+0·513	+256	1·64	5·71	+0·838	+257
	1·67	5·14	0		1·64	5·11	0	
	Me_2CH·CN. *Treatment* (a), *with* μ_{res} *along* C–CN				Me_2CH·CN. *Treatment* (b), *with* μ_{ind} *along* C–Me			
MeCN	3·64	8·87	+3·590		3·64	8·87	+3·517	
	1·75	7·06	+0·466	+208	1·75	7·06	+0·870	+192
	1·75	7·73	0		1·75	7·73	0	
Me_3C·CN	4·03	9·25	+3·603		4·03	9·25	+3·543	
	1·54	6·86	+0·351	+296	1·54	6·86	+0·757	+278
	1·54	7·52	0		1·54	7·52	0	
Interpolated	3·88	9·10	+3·599		3·95	9·17	+3·539	
	1·61	6·93	+0·386	+263	1·57	6·89	+0·773	+262
	1·61	7·59	0		1·57	7·55	0	

* Listed, here and elsewhere, in descending order as $b_{\mathrm{L}}^{\mathrm{CCN}}$, $b_{\mathrm{T}}^{\mathrm{CCN}}$, and $b_{\mathrm{V}}^{\mathrm{CCN}}$ ($= b_{\mathrm{T}}^{\mathrm{CCN}}$). † Listed, here and elsewhere, in descending order as b_1, b_2, b_3. ‡ Listed, here and elsewhere, in descending order as μ_1, μ_2, μ_3.

TABLE 7

Polarisabilities of the C–CN group

Molecule	MeCN	$MeCH_2$·CN	Me_2CH·CN	Me_3C·CN
$b_{\mathrm{L}}^{\mathrm{CCN}}$	$3{\cdot}6_4$	3·8	3·9	$4{\cdot}0_3$
$b_{\mathrm{T}}^{\mathrm{CCN}}$	$1{\cdot}7_5$	$1{\cdot}6_5$	1·6	$1{\cdot}5_4$
($b_{\mathrm{L}}^{\mathrm{CCN}} - b_{\mathrm{T}}^{\mathrm{CCN}}$)	1·9	2·2	2·3	2·5

TABLE 8

Evaluation of ${}_{\mathrm{m}}K$ (calc.) for $MeCH_2$·CN and Me_2CH·CN by the alternative approach

		Treatment (a), *with* μ_{res} *along* C–CN		*Treatment* (b), *with* μ_{ind} *along* C–Me	
Molecule	b_1, b_2, b_3	μ_1, μ_2, μ_3	$10^{12}{}_{\mathrm{m}}K$ (calc.)	μ_1, μ_2, μ_3	$10^{12}{}_{\mathrm{m}}K$ (calc.)
$MeCH_2$·CN	7·39	+3·528		+3·522	
	5·31	−0·136	+272	+0·225	+271
	5·53	0		0	
Me_2CH·CN	9·22	+3·618		+3·612	
	6·95	−0·127	+298	+0·283	+296
	7·39	0		0	

have been calculated by addition of bond-polarisability tensors and diagonalisation of the resulting matrix, by use of standard procedures.[1a,18] Such calculations have been carried out with C–CN group polarisabilities obtained (i) from acetonitrile, (ii) from t-butyl cyanide and (iii) by interpolation in the results of (i) and (ii), with the requirements that ($b_{\mathrm{L}}^{\mathrm{CCN}} + 2b_{\mathrm{T}}^{\mathrm{CCN}}$) is constant and that ${}_{\mathrm{m}}K$ (calc.) $=$ ${}_{\mathrm{m}}K$ (obs.). These polarisability values, in conjunction with the dipole-moment components, μ_1, μ_2, μ_3, along the axes of b_1, b_2, b_3, respectively, yield values of ${}_{\mathrm{m}}K$ (calc.), which may be compared with the observed data.

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[18] Eckert and Le Fèvre, *J.*, 1962, 1081.

This procedure has been carried out (see Table 6) for both treatments (a) and (b) of the dipole-moment direction, as discussed above.

The values of ${}_{\rm m}K$ (calc.) in Table 6 are to be compared with the ${}_{\rm m}K$ (obs.) for propionitrile and isobutyronitrile of $+256 \times 10^{-12}$ and $+262 \times 10^{-12}$, respectively. From the results obtained with the interpolated bond-polarisabilities, it may be concluded with considerable confidence that polarisabilities of the C–CN group in the series, acetonitrile, propionitrile, isobutyronitrile, and t-butyl cyanide, are as in Table 7. The regular gradation of anisotropy is to be noted.

An alternative approach to the interpretation of results for the aliphatic nitriles has also been attempted. This involves the assumption that the C–CN group has the same polarisability in propionitrile, isobutyronitrile, and t-butyl cyanide as in acetonitrile, and that the polarisability of a C–C bond adjacent to the C–CN group is different from its usual value.[1a] An estimate of $b^{\rm CC}$ (adjacent to CCN), obtained simply from b_1, b_2, b_3 of t-butyl cyanide with the assumption that $b^{\rm CCN}$ is as in acetonitrile, is $b_{\rm L}^{\rm CC} = 0{\cdot}33$, $b_{\rm T} = 0{\cdot}58$. The validity of this estimate may be tested by inserting the new $b^{\rm CC}$'s together with $b^{\rm CCN}$ values extracted from acetonitrile, into calculations for propionitrile and isobutyronitrile. The values of ${}_{\rm m}K$ (calc.) obtained in this way are as in Table 8.

Comparison of the results of Table 8 with the observed ${}_{\rm m}K$'s of propionitrile and isobutyronitrile ($+256 \times 10^{-12}$ and $+262 \times 10^{-12}$, respectively) is not unsatisfactory, agreement being to within 6 and 13%, respectively This alternative interpretation of results may, therefore, be equally valid.

Polarisabilities of $CH_2(CN)_2$ *and* $ClCH_2{\cdot}CN$.—For malononitrile, ${}_{\rm m}K$ (calc.)'s have been evaluated, assuming the molecular geometry already indicated (∠CCC = 114°, with CCN linear), the usual C–H bond polarisability values,[1a] and C–CN group polarisabilities extracted (i) from acetonitrile and (ii) from t-butyl cyanide. Calculations have also been carried out for ∠CCC = 118°. The results of such calculations are in Table 9.

The ${}_{\rm m}K$ (calc.)'s of Table 9 differ markedly from the observed ${}_{\rm m}K$ (-72×10^{-12}), a CCC bond angle as great as 118° being insufficient to reconcile ${}_{\rm m}K$ (calc.) with ${}_{\rm m}K$ (obs.). The suggestion [19] that the CCN group is slightly bent by 3° 40′ ± 2° 54′ might possibly account for this deviation. Alternatively, the large negative exaltation of $R_{\rm D}$ ($-1{\cdot}0$ c.c.) may suggest some electronic mechanism not allowed for in estimating ${}_{\rm m}K$ (calc.). Further calculations show that experimental results are consistent with a bond angle of 114° and an exaltation of polarisability of $-0{\cdot}3$ along b_1, or of $+0{\cdot}6$ along b_2. Again, the poor agreement between ${}_{\rm m}K$ (calc.) and ${}_{\rm m}K$ (obs.) may be due to solute–solvent interactions in solutions of malononitrile in benzene. Hence, for malononitrile, a definite conclusion is not justified.

TABLE 9

Evaluation of ${}_{\rm m}K$ (calc.) for $CH_2(CN)_2$

		CCC = 114°		CCC = 118°	
Source of $b^{\rm CCN}$	μ_1, μ_2, μ_3	b_1, b_2, b_3	$10^{12}{}_{\rm m}K$ (calc.)	b_1, b_2, b_3	$10^{12}{}_{\rm m}K$ (calc.)
MeCN	3·56	5·90	−27	5·78	−52
	0	7·44		7·56	
	0	4·78		4·78	
$Me_3C{\cdot}CN$	3·56	5·84	−33	5·68	−66
	0	7·86		8·02	
	0	4·36		4·36	

For chloroacetonitrile, ${}_{\rm m}K$ (calc.)'s have been evaluated, assuming the bond angle and dipole-moment direction already indicated, the usual C–H bond polarisability values,[1a] and C–CN and C–Cl polarisabilities obtained (i) from acetonitrile and methyl chloride,[1a]

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[19] Hirota and Morino, *Bull. Chem. Soc. Japan*, **1960**, **33**, 705.

respectively, (ii) from t-butyl cyanide and t-butyl chloride,[1a] respectively, and (iii) by interpolation in the results of (i) and (ii) with respect to relative change of anisotropy of C–CN and C–Cl. The results of these calculations are in Table 10.

TABLE 10

Evaluation of ${}_{\mathrm{m}}K$ (calc.) for $ClCH_2{\cdot}CN$

Source of b^{CCN}, b^{CCl}	b^{CCN}	b^{CCl}	b_1, b_2, b_3	μ_1, μ_2, μ_3	$10^{12}{}_{\mathrm{m}}K$ (calc.)
MeCN, MeCl	3·64	3·18	7·35	+2·105	+72
	1·75	2·20	5·98	+2·095	
	1·75	2·20	5·23	0	
$Me_3C{\cdot}CN$, Me_3CCl	4·03	3·95	7·74	+1·380	+47
	1·54	1·58	5·92	+2·630	
	1·54	1·58	4·40	0	
Interpolated	3·87	3·73	7·64	+1·634	+56
	1·62	1·92	6·06	+2·480	
	1·62	1·92	4·82	0	

The results of Table 10 are to be compared with an observed ${}_{\mathrm{m}}K$ of $+57 \times 10^{-12}$. Although the above treatment is far from rigorous, the interpolated values of b^{CCN} and b^{CCl} probably represent the most reliable estimates which can be obtained for this molecule. The interpolated values of b^{CCN} obtained for chloroacetonitrile are of the same order as those estimated for isobutyronitrile (Table 7), in contrast to trichloroacetonitrile, for which b^{CCN} was as in acetonitrile (Table 5).

C–CN *Polarisability in* $C_6H_5{\cdot}CN$.—For this molecule, a knowledge of the ${}_{\mathrm{E}}P$ (30·2 c.c.[2a]), light-scattering data (Le Fèvre and Rao [20] find $10^3{}_{\infty}\delta_2{}^2 = 75{\cdot}22$), and the ${}_{\infty}({}_{\mathrm{m}}K_2)$ and μ (Table 2) permit molecular polarisability semi-axes, b_1, b_2, b_3, to be evaluated unambiguously. The values of quantities derived in such a treatment are:

$(b_1 + b_2 + b_3)$	$\Sigma(b_i - b_j)^2$	$(2b_1 - b_2 - b_3)$	b_1	b_2	b_3
35·91	9·70	12·89	16·27	11·34	8·30

The above b's are to be compared with $b_1 = 16{\cdot}16$, $b_2 = 11{\cdot}60$, and $b_3 = 8{\cdot}15$, as reported previously.[20] Subtraction of the appropriate polarisability components of the C_6H_5 group [21] gives $b_{\mathrm{L}}^{\mathrm{CCN}} = 5{\cdot}71$, $b_{\mathrm{T}}^{\mathrm{CCN}} = 0{\cdot}78$, $b_{\mathrm{V}}^{\mathrm{CCN}} = 1{\cdot}58$, compared with the previously reported [20] values of 5·7, 1·1, $1{\cdot}4_5$, respectively. It is found that $b_{\mathrm{V}}^{\mathrm{CCN}}$ is greater than $b_{\mathrm{T}}^{\mathrm{CCN}}$, as observed in aromatic halides.[1a] The anisotropy, $(2b_{\mathrm{L}} - b_{\mathrm{T}} - b_{\mathrm{V}})/2$, of the C–CN group in benzonitrile is 4·5, which is much greater than that found for aliphatic nitriles [compare the $(b_{\mathrm{L}} - b_{\mathrm{T}})$'s of Table 7]. This may be attributed to resonance interactions between the π-electrons of the phenyl and cyano-groups.

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UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA. [*Received, July 3rd*, 1964.]

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[20] Le Fèvre and Rao, *J.*, 1958, 1465.
[21] Aroney and Le Fèvre, *J.*, 1960, 3600.