Electric Dipole Moments of Some Acrylonitriles, Allyl Cyanides, and Alicyclic Nitriles

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The electric dipole moments of 24 nitriles have been measured in benzene solution at 25·0 °C. The results for acrylonitrile, its *cis*- and *trans*-substituted derivatives, and alicyclic nitriles are discussed in terms of group and induced moments while those for three allyl cyanides are employed to indicate preferred molecular conformations. The greatest increment in dipole moment arises from the presence of a *trans*-CH_2–C=C–CN unit.

THE cyano-group is a valuable substituent for the elucidation of molecular structures by the dipole moment method because (a) it is linear and (b) it possesses a large group moment. The investigations reported here show the contributions to the dipole moment of a molecule of a carbon–carbon double bond, both conjugated and non-conjugated with the cyano-group, and also the consequences of methyl substitution of this double bond. These results will be of value when analysing the electric dipole moments of more complex molecules.

EXPERIMENTAL AND RESULTS

The electric dipole moments were determined as described previously.[1] The measured properties of the solutions at 25·0 °C are deposited with the N.L.L. as Supplementary Publication SUP No. 20645 (5 pp.) † and the polarisation data and dipole moments are in the Table; the symbols have their usual meanings. Because of the relatively high dipole moments and small molecular weights low solute concentrations were employed. The high dipole moment means that errors from any inadequacy in the allowance for atom polarisation will be minimal.

Preparation and Purification of Compounds.—Each compound was extensively purified by fractionation and/or g.l.c. immediately before its dipole moment was determined. Its purity was verified by analytical g.l.c. (Carbowax 20M or silicone oil columns; flame-ionisation detector) and by i.r., u.v., and ^1H n.m.r. spectroscopy. Commercial samples of the following were purified: acetonitrile (B.D.H.), b.p. 80°; propionitrile (B.D.H.), b.p. 97°; n-butyronitrile (B.D.H.), b.p. 118°; acrylonitrile (Koch–Light), b.p. 76·5°, all at 760 mmHg; *trans*-cinnamonitrile (Koch–Light), b.p. 86° at 0·5 mmHg; benzonitrile (Koch–Light), b.p. 56° at 7·0 mmHg; 4-cyanocyclohexene (Emmanuel), b.p. 37° at 0·7 mmHg. A mixture of *cis*- and *trans*-crotononitrile (Koch–Light) was dried over calcium chloride and the isomers separated by preparative g.l.c. (7 ft Carbowax column; 60 °C). 3,3-Dimethylacrylonitrile was prepared [2] by the very slow addition of concentrated sulphuric acid to a stirred mixture of isobutyraldehyde and sodium cyanide solution at 10 °C and leaving for 20 h. The isobutyraldehyde cyanohydrin, isolated from an ether extract of this mixture, was refluxed with anhydrous P_2O_5 and the product isolated by fractional distillation followed by preparative g.l.c. (15 ft Carbowax column; 100 °C). *cis*- and *trans*-1-Cyanobuta-1,3-dienes were prepared [3] by the pyrolysis of crotonaldehyde cyanohydrin benzoate at 575 °C in the presence of 4-t-butylcatechol as a polymerisation inhibitor. The products were isolated by washing with sodium carbonate solution and water, drying and fractionating; the two

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† For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue 20. Items less than 10 pp. are sent as full size copies.

[1] C. W. N. Cumper, A. A. Foxton, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 1964, 430.

[2] R. F. B. Cox and R. T. Stormont, *Org. Synth.*, 1943, **2**, 7.

[3] H. R. Snyder, J. M. Stewart, and R. L. Myers, *J. Amer. Chem. Soc.*, 1949, **71**, 1055.

isomers were separated by g.l.c. (7 ft Carbowax column; 90 °C). 3-Cyanopropene, prepared[4] from dry 3-bromopropene and cuprous cyanide, was isolated by distillation and purified by fractionation (b.p. 56° at 78 mmHg). Crotyl bromide (Koch–Light) was a mixture of 1-bromobut-2-ene (85%) and 3-bromobut-1-ene (15%) so that two products were obtained by reaction of this with dry cuprous cyanide. Fractionation gave fractions of b.p. 48—50° and 50° at 25 mmHg which were purified by distillation on a spinning band column and by preparative g.l.c. 1-Cyanobut-2-ene and 3-cyanobut-1-ene were identified by their ^{1}H n.m.r. spectra. 4-Cyanobiphenyl was prepared[5] from the corresponding bromobiphenyl and recrystallised from ethanol, m.p. 86·5°. Cyanocyclohexane, b.p. 58° at 0·8 mmHg, was prepared[6] from cyclohexanecarboxylic acid and 1-cyanocyclohexene, b.p. 62° at 6 mmHg, from cyclohexanone.[7] 2-Methylcyclohexanone cyanohydrins, from 2-methylcyclohexanone and acetone cyanohydrin,[8] were separated by crystallising out the *cis*-isomer which was then converted into its acetate with acetic anhydride, purified, and pyrolysed[9] at 500 °C. Cyanide ion was removed with silver nitrate, the mixture filtered, extracted with ether, washed with aqueous potassium carbonate, and dried. Fractionation gave two isomeric methylcyclohexenecarbonitriles and the 1-cyano-2-methylcyclohexene (identified by n.m.r. spectroscopy) was purified by fractionation on a spinning-band column, b.p. 61° at 0·5 mmHg. 1-Cyano-6-methylcyclohexene was prepared[10] by dehydration of the isomeric 2-methylcyclohexanone cyanohydrins, from 2-methylcyclohexanone and sodium cyanide in the presence of sodium bisulphite. The cyanohydrins in pyridine were added to a phosphorus oxychloride–pyridine mixture at 0 °C; the temperature slowly increased and the mixture was refluxed for 1 h. The mixture was poured on ice, extracted with ether, washed, dried, and fractionated. The mixed isomers obtained were mainly 1-cyano-6-methylcyclohexene and this was isolated and purified by spinning-band fractionation and g.l.c. (7 ft Carbowax column; 150 °C). Cyanocyclopentane was prepared from bromocyclopentane by Friedman and Shechter's method[11] for the corresponding chloro-compound. Final purification was by fractionation (b.p. 72° at 26 mmHg) and g.l.c. (7 ft silicone column; 100 °C). 1-Cyanocyclopentene[12] was made in the same manner as the cyclohexene and purified by fractionation and chromatography (7 ft Carbowax column; 130 °C). 1-Cyano(methyl)cyclopentenes were prepared[10,13] by the method employed for 1-cyano-6-methylcyclohexene. The two isomers, 2-methyl- and 5-methyl-1-cyanocyclopentene, were separated by spinning-band distillation and g.l. (7 ft Carbowax; 90 °C and a silicone gum column; 100 °C), and identified by their n.m.r. spectra.

Polarisation data and dipole moments (μ) at 25·0 °C in benzene solution

Compound	α	β	γ	P_T/cm^3	R_D/cm^3	μ/D	Lit. values μ/D
Acetonitrile	$32{\cdot}3_9$	0·120	−0·65	265·4	10·2	3·53	3·50, 3·47 [a]
Propionitrile	$24{\cdot}8_2$	0·179	0·68	278·4	(28·5)	3·50	3·60 [a]
Butyronitrile	$18{\cdot}7_1$	0·107	−0·45	268·8	19·5	3·50	3·60 [a]
Acrylonitrile	$27{\cdot}2_4$	0·136	−0·30	291·9	16·8	3·67	3·51 [b]
cis-Crotononitrile	$21{\cdot}8_8$	0·029	−0·23	299·4	20·1	3·70	
trans-Crotononitrile	$26{\cdot}5_1$	0·141	−0·27	359·9	21·9	4·07	
3,3-Dimethylacrylonitrile	$21{\cdot}7_0$	0·076	−0·30	360·3	24·4	4·06	
trans-Cinnamonitrile	$15{\cdot}3_6$	−0·186	0·33	409·9	44·4	4·23	4·17 † [c]
trans-1-Cyanobuta-1,3-diene	$21{\cdot}3_6$	0·087	0·06	350·9	29·8	3·96	
cis-1-Cyanobuta-1,3-diene	$19{\cdot}6_0$	0·048	−0·25	323·5	24·2	3·83	
3-Cyanopropene	$18{\cdot}5_7$	0·058	−0·38	258·2	18·8	3·42	
trans-1-Cyanobut-2-ene	$17{\cdot}0_8$	0·086	−0·33	290·2	24·1	3·61	
3-Cyanobut-1-ene	$16{\cdot}4_1$	0·085	−0·33	279·8	24·1	3·54	
Benzonitrile	$17{\cdot}1_1$	−0·059	0·15	364·9	35·8	4·01	4·05 [d]
4-Cyanobiphenyl	$11{\cdot}7_2$	−0·273	0·46	447·1	61·4	4·34	4·33 [e]
Cyanocyclohexane	$14{\cdot}1_1$	0·018	−0·13	327·2	34·5	3·79	
1-Cyanocyclohexene	$17{\cdot}9_1$	−0·113	0·12	393·7	34·9	4·19	
1-Cyano-2-methylcyclohexene	$16{\cdot}1_5$	−0·073	−0·09	406·6	35·9	4·26	
1-Cyano-6-methylcyclohexene	$15{\cdot}2_9$	−0·134	−0·11	384·7	33·3	4·15	
4-Cyanocyclohexene	$12{\cdot}9_1$	−0·141	−0·09	292·1	29·6	3·58	
Cyanocyclopentane	$16{\cdot}0_9$	−0·074	−0·14	318·1	27·4	3·77	
1-Cyanocyclopentene	$18{\cdot}2_2$	−0·069	−0·15	348·8	26·7	3·97	
1-Cyano-2-methylcyclopentene	$17{\cdot}5_3$	−0·077	−0·10	392·3	31·6	4·20	
1-Cyano-5-methylcyclopentene	$16{\cdot}4_2$	0·008	−0·18	372·2	32·5	4·08	

† In 1,4-dioxan solution.

[a] Ref. 20. [b] M. T. Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 2544. [c] H. L. Goebel and H. H. Wenske, *J. Amer. Chem. Soc.*, 1938, **60**, 697. [d] C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 1960, 4723. [e] K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 1951, 2807.

DISCUSSION

The electric dipole moments of three alkyl cyanides were determined to establish the cyano-group moment in benzene solution. The dipole moment of MeCN (3·5 D) would be expected to be slightly smaller than those of EtCN and PrCN whereas the experimental

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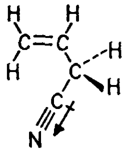
result is 0·03 D greater. This can be attributed to a solvent effect; the Buckingham–Le Fèvre equation[14] predicts dipole moments of 3·95, 4·15, and 4·18 D respectively in the vapour phase compared to experimental values[15] of 3·94, 4·00, and 4·05 D. We shall take the cyano-group moment as 3·50 D in benzene solution.

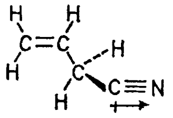
Acrylonitriles.—Acrylonitrile itself has a dipole moment of 3·67 D; with a $C{=}\widehat{C}{-}CN$ bond angle[16] of 122·6° this would require an induced moment of 0·30 D in the double bond from the attached cyano-group. When one of the β-hydrogen atoms in acrylonitrile is replaced by a methyl group there will be a Me–C bond moment[17] of *ca.* 0·3 D between the differently hybridised carbon atoms. This means that the calculated dipole moment[*] is decreased to 3·60 D for *cis*-crotononitrile and increased to 3·97 D for the *trans*-isomer; in each case these are 0·10 D less than the experimental values. The discrepancy might arise from the electric field of the large cyano-group moment inducing moments in the methyl group. Employing the equations of Smallwood and Herzfield[19] to estimate the induced moments and locating the 'point-dipole' at the centre of the C≡N bond and the polarisation centre at the methyl carbon atom, then such induced moments would further reduce the calculated moment for *cis*-crotononitrile and only increase that for the *trans*-isomer by a much smaller amount. A more likely explanation is that the inductive effect of the methyl group permits a greater polarisation and induced moment in the C=C bond. If this component is increased to 0·47 D the calculated dipole moments become 3·69 and 4·08 D for *cis*- and *trans*-crotononitrile respectively. The small effect upon the resultant dipole moment of replacing the β-hydrogen atom *cis* to the cyano-group in acrylonitrile by a methyl group is substantiated by the corresponding substitution in *trans*-crotononitrile to give 3,3-dimethylacrylonitrile; the dipole moment is only altered by 0·01 D. With a moment of 0·47 D induced in the C=C bond the calculated dipole moment of this molecule is 4·00 D, which is 0·06 D lower than observed.

In *trans*-cinnamonitrile a Ph–C group moment of 0·56 D is required to account for the increase in the dipole moment of acrylonitrile from 3·67 D to its experimental value of 4·23 D. Unfortunately we were unable to isolate the *cis*-isomer. An increase of the dipole moment of acrylonitrile to that of *trans*-1-cyanobuta-1,3-diene (3·96 D) requires an extra moment of 0·47 D in the direction of the additional ethylenic bond but for the *cis*-isomer (3·83 D) the increment is only 0·26 D. In each of these cases the component moments in the acrylonitrile residue were assumed to be unaltered.

Allyl Cyanides.—As expected, when the ethylenic residue is no longer able to conjugate with the cyano group its effect upon the dipole moment is less. That of 3-cyanopropene is actually 0·08 D less than for the saturated alkyl cyanides. Two possible conformations for this molecule are (I) and (II). In conformation (I)



(I)



(II)

the moment induced in the C=C bond by the cyano-group moment would produce a small reduction in the dipole moment of the molecule whereas in (II) it would be increased. Although rotation about the C–C(CN) bond almost certainly occurs, conformation (I) would appear to predominate; this seems likely since the vinylic hydrogen atom would be staggered between those of the methylene group. Substitution of one of these methylene hydrogen atoms by a methyl group to give 3-cyanobut-1-ene increases the dipole moment by 0·12 D, which is not unreasonable; substitution of a β vinylic hydrogen atom to form *trans*-1-cyanobut-2-ene increases the dipole moment by 0·19 D which is only half the increase observed between the conjugated acrylonitrile and *trans*-crotononitrile molecules. The predominance of a conformation analogous to (I) would also explain why 3-chloropropene (1·79 D) has a dipole moment (0·17 D) less than that of propyl chloride.[20]

Alicyclic Nitriles.—The dipole moments of cyanocyclohexane (3·97 D), cyanocyclopentane (3·77 D), and the literature value[21] for cyanocyclopropane (3·75 D) indicate a possible slight decrease with ring size. The small differences between these values and those of t-butyl cyanide (3·65 D)[20] and acetonitrile (3·53 D) may be due to induced moments.

The mesomeric moment in benzonitrile (μ 4·01 D) increases the dipole moment over that of the saturated cyanocyclohexane by 0·22 D and in 4-cyanobiphenyl it is increased by a further 0·33 D. The aromatic ring might have been expected to cause a greater increment because a single localised carbon–carbon double bond attached to the cyano-group (acrylonitrile) gives a 0·17 D increase over that of the saturated cyanide and with the two conjugated double bonds in the *cis*- and *trans*-1-cyanobuta-1,3-dienes the increases are 0·33 and 0·46 D respectively. The greatest increment with the noncyclic nitriles resulted from the presence of a *trans*-Me–C=C–(CN) group and the effect of this system is also

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[*] Taking the $C{=}\widehat{C}{-}CN$ and $Me{-}\widehat{C}{-}C$ bond angles as 123·2 and 124·3° respectively for the *cis*-isomer and 121·9 and 124·3° for the *trans*-isomer.[18]

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evident in the alicyclic nitriles. 1-Cyanocyclohexene has a moment 0·4 D greater than the saturated nitrile, and it is even 0·18 D greater than that of benzonitrile. The *cis*-methyl group in 1-cyano-2-methylcyclohexene makes relatively little difference (*cf.* acrylonitrile and *cis*-crotononitrile) and in 1-cyano-6-methylcyclohexene the methyl group even reduces the resultant dipole moment by 0·04 D. 4-Cyanocyclohexene, in which the double bond cannot conjugate with the cyano-group, has a dipole moment closer to those of the saturated alkyl cyanides than to the corresponding saturated alicyclic compound.

The dipole moments of the five-membered ring molecules studied were 0·02—0·07 D less than for the corresponding six-membered rings with the exception of 1-cyanocyclopentene. The difference in this case (0·22 D) is unexpected and we cannot offer an explanation; it would not appear to be due to experimental errors.

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