Structural Effects on the Electrochemisty and Charge Distribution of Mono-, Di-, and Tri-cyanovinyl Aromatic Compounds

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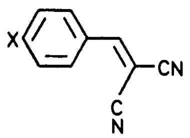
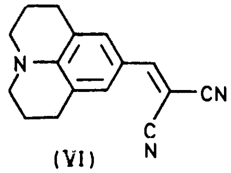
The effect on electrochemical behaviour and electronic charge distribution was examined for a series of 12 vinyl aromatic compounds having the following structural variations: (a) number of cyano-groups attached to the vinyl double bond, (b) substitution *para* to the vinyl group, and (c) separation between *para*-substituent and the vinyl group. The radical anion formed in the first one-electron reduction step can either accept a second electron or undergo an irreversible dimerization. Oxidation waves were seen only with those compounds having an amino nitrogen atom *para* to the vinyl group. Trends in half-wave potentials caused by variation in structure are correlated by means of the Hammett–Zuman and molecular orbital approaches. Due to the strong electron-withdrawing power of the cyano-substituted vinyl group, considerable intramolecular donor–acceptor interaction occurs between the ends of the molecules. This is seen in the measured molecular dipole moments and reflected in the nitrile stretching frequencies and proton chemical shifts. Finally, the efficiences for generation of charge carriers in the compounds as measured by xerographic discharge are related to their solution reduction potentials.

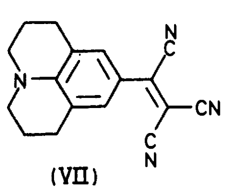
THE characterization of the series of mono-, di-, and tri-cyanovinyl aromatic compounds (I)—(XII) receives its impetus from the possibilities for electrophotographic application shown by members of this class of compounds.[1] Recent reports from these laboratories describe changes of orders of magnitude in charge carrier mobility in carbazole polymers [2] and similar changes in the efficiency of photostimulated charge injection by azo-dyes [3] caused by structural variations on a basic molecular framework. Our continuing interest in the electrical properties of organic solids and the belief that the key to their behaviour lies in understanding the electronic structure of the isolated molecules led us to an examination of compounds (I)—(XII).



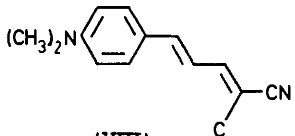
(I) X = $(CH_3)_2N$
(II) X = CH_3O
(III) X = H
(IV) X = Cl
(V) X = NO_2



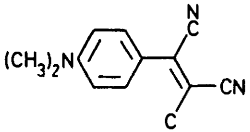
(VI)



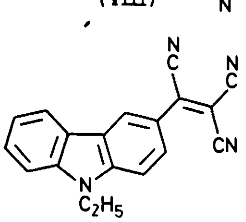
(VII)



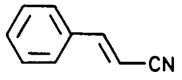
(VIII)



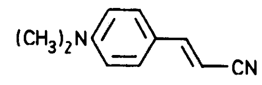
(IX)



(X)



(XI)



(XII)

Solution electrochemical techniques provide a convenient means to study the effect of such structural variations on molecular energy levels, since it is known that polarographic reduction and oxidation potentials may be related to the corresponding gas-phase electron affinities [4] and ionization potentials,[5,6] respectively. While obtaining this information and relating it to observed behaviour in the solid state provided a major impetus for our studies, the present series of compounds also afforded the opportunity to examine the effect of intramolecular donor–acceptor interactions on charge distributions as evidenced by dipole moments and i.r. and n.m.r. spectral data.

RESULTS AND DISCUSSION

Voltammetry of Benzylidenemalononitrile (III).—The voltammetry of benzylidenemalononitrile in acetonitrile (AN) is typical of the behaviour seen in the present series. The polarogram consists of two reduction waves located at —1.07 and —1.74 V *vs.* s.c.e. This compares to half-wave potentials of —0.92 and —1.47 V *vs.* s.c.e. previously reported for (III) in basic aqueous methanol.[7]

The electrode process occurring at the potential of the first wave is a reversible one-electron transfer followed by irreversible dimerization. This conclusion is in agreement with recent findings of Nadjo and Saveant [8,9] for compounds of this type based on linear sweep voltammetry, and is supported by the following evidence

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[1] Ger. Offen. 2,513,150/1976; 2,513,167/1976.

[2] D. J. Williams, W. W. Limburg, J. M. Pearson, A. O. Goedde, and J. F. Yanus, *J. Chem. Phys.*, 1975, **62**, 1501.

[3] P. J. Cressman, G. C. Hartmann, J. E. Kuder, F. D. Saeva, and D. Wychick, *J. Chem. Phys.*, 1974, **61**, 1714.

[4] M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Amer. Chem. Soc.*, 1970, **92**, 5555.

[5] L. L. Miller, G. C. Nordblom, and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916.

[6] E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, 1963, **85**, 2124.

[7] J. E. Kuder, D. Wychick, and P. Zuman, *J. Electroanalyt. Chem.*, 1976, **71**, 297.

[8] E. Lamy, L. Nadjo, and J. M. Saveant, *J. Electroanalyt. Chem.*, 1973, **42**, 189.

[9] L. Najdo, J. M. Saveant, and D. Tessier, *J. Electroanalyt. Chem.*, 1975, **64**, 143.

obtained for (III). Controlled potential electrolysis on the plateau of the first reduction wave of (III) indicates the transfer of one electron at this potential (duplicate runs $n = 0.99$ and 0.95). Evidence as to the nature of the electron transfer step is to be found in the shape of the polarographic wave. Thus, for reversible charge transfer followed by irreversible dimerization,[10] a straight line with slope $-RT/3n\mathrm{F}$ is obtained from a plot of E *vs.* ln $[i^3/i_d(i_d - i)^2]$, where i is the current corresponding to any potential E on the cathodic wave and i_d is the limiting current. Analysing the first reduction wave of (III) by this relationship leads to a calculated value of $n = 1.12$, in satisfactory agreement with the value $n = 1$ obtained by coulometry. By comparison, a plot of E *vs.* log $[i/(i_d - i)]$ gives for simple electron transfer a straight line with slope $-0.059/n$ for a reversible wave or $-0.059/\alpha n$ for an irreversible wave.[11] Applying this latter test to the first wave of (III) leads to a value of n of 1.32 or, assuming an irreversible process and the coulometric value of $n = 1$, the unlikely[12] value of $\alpha > 1$, in either case, less reasonable than the electron transfer–dimerization mechanism suggested by the former analysis.

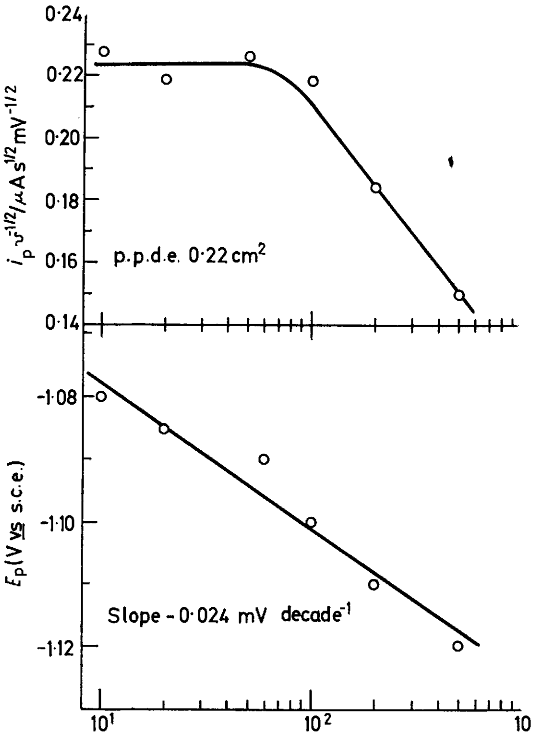

FIGURE 1 Current function and peak potential for (II) as a function of sweep rate

Examination of (III) by cyclic voltammetry (c.v.) shows only a cathodic peak for the first reduction step, the corresponding anodic peak upon reversal of scan direction being absent up to sweep rates of 0.5 V s^{-1}. The dependence of the current function $i_p/v^{1/2}$ (i_p is the peak current) on sweep rate v is shown in Figure 1. The current function is constant at low sweep rates, but begins to decrease at higher rates, in keeping with charge transfer followed by irreversible chemical reaction.[13] In addition, the peak potential E_p undergoes a shift to more negative potentials of 24 mV for a tenfold increase in v. This shift is in satisfactory agreement with the theoretical value of 20 mV decade^{-1} derived by Nadjo and Saveant[8] for the dimerization mechanism.

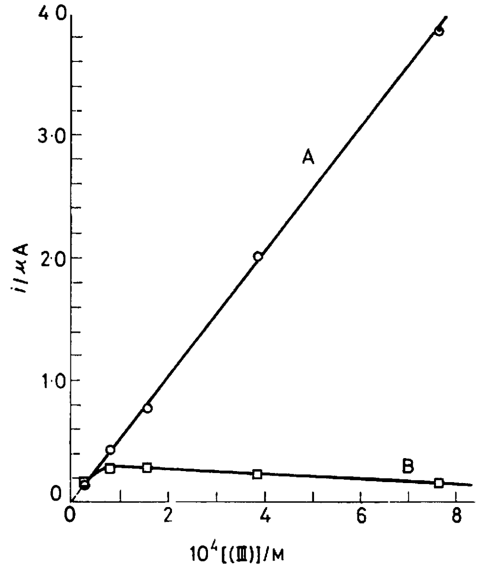

FIGURE 2 Concentration dependence of the limiting current for the first A and second B reduction waves of (III)

Finally, as shown in Figure 2, the relative heights of the two waves are dependent on sample concentration. At low concentration the two waves are of equal height, but while the limiting current of the first wave increases linearly with concentration, that of the second wave initially increases and then approaches zero at higher concentration. Presumably the second reduction wave corresponds to the uptake of a second electron by the initially formed radical anion to give the corresponding dianion. The decrease in the height of the second wave with increasing sample concentration is then due to increased importance of the radical coupling step described above, which results in the formation of an electroinactive dimeric species and thus lowers the proportion of monomer available for a second electron transfer at the electrode.

No oxidation wave was seen when solutions of (III) were examined with a rotating platinum disc electrode (r.p.d.e.).

Structural Correlations of Redox Behaviour.—The

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[10] J. Koutecky and V. Hanus, *Coll. Czech. Chem. Comm.*, 1955, **20**, 124.

[11] L. Meites, 'Polarographic Techniques,' Wiley–Interscience, New York, 1965, 2nd edn., ch. 4.

[12] H. H. Bauer, *J. Electroanalyt. Chem.*, 1968, **16**, 419.

[13] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1965, **37**, 178.

polarographic reduction data for compounds (I)—(XII) are presented in Table 1. In general, the compounds show two reduction waves separated by 0.5—0.7 V. The diffusion current constant I_{d} for the first waves have an average value of 2.61 ± 0.50, as expected for a one-electron reduction in AN.[14] For the reason cited in the preceding paragraph, I_{d} values are not reported for the second waves.

The compounds may be divided into two classes based on their log plot analysis and c.v. response. As already indicated, a plot of E *vs.* log $[i/(i_{\mathrm{d}} - i)]$ is not strictly appropriate to the proposed reduction mechanism. It serves for the present purposes, however, to distinguish the two types of response. The tricyanovinyl compounds (VII)—(X) have log plot slopes very close to 59 mV for the first wave and show reversible c.v.[15] behaviour with separation of 0.07 V between cathodic and anodic peaks. From this, it may be inferred that when the vinyl group is completely substituted, the radical coupling step is inhibited, and simple reversible one-electron transfer is observed. (Tetracyanoethylene similarly undergoes reversible one-electron reduction.[16]) In contrast, the remainder of the compounds have log plot slopes considerably less than 59 mV and are irreversible in the c.v. experiment. It is not possible to make the same division into two classes based on the log plot analyses for the second wave. These show considerable variation in magnitude, but are, in general, accompanied by an irreversible e.v. response.

TABLE 1

Electrochemical data, HMO-ω energy levels, dipole moments, and nitrile stretching frequencies

	Polarographic reduction data				Polarographic oxidation data									
									HOMO and LUMO energies [h]		Dipole moments			
Compound	$E_{1/2}$ (V *vs.* s.c.e.)	Slope of log plot [a] (mV)	I_{d} [b]	C.v.[c]	$E_{1/2}$ (V *vs.* s.c.e.)	Slope of log plot [e] (mV)	$i_{\mathrm{L}}C\omega^{1/2}$ [f]	C.v.[g]	E_{HOMO},β	E_{LUMO},β	$\mu_{\mathrm{exp.}}$/D This work	Lit.	$\mu_{\mathrm{calc.}}$/D (vector addn)	Nitrile stretching frequencies $\bar{\nu}_{\mathrm{CN}}$/cm^{-1}
(I)	−1.34	44	1.98	Irrev	+1.13	68	31.9	Rev	0.483	−0.454	8.70	8.80 [i]	6.09	2 214
	−1.92	54		*d*										
(II)	−1.20	51	2.50	Irrev							6.26	6.37 [i]	5.58	2 224
	−1.83	76		*d*										
(III)	−1.07	45	3.11	Irrev					0.748	−0.395	5.24	5.28 [i]	5.24	2 226
	−1.74	151		*d*										
(IV)	−0.98	44	2.89	Irrev							4.18	4.17 [i]	4.65	2 230
	−1.64	66		*d*										
(V)	−0.58	56	2.73	Irrev							3.05	3.10 [i]	4.75	2 235
	−0.84	90		Irrev										
	−1.14	60		Rev										
(VI)	−1.41	35	3.01	Irrev	+0.89	52	31.0	Rev	0.456	−0.463	9.43			2 215
	−2.00	47		*d*										
(VII)	−0.72	59	3.30	Rev	+1.06	46	30.0	Rev	0.463	−0.316	10.23			2 211
	−1.22	100		Irrev										
(VIII)	−1.11	39	2.31	Irrev	+0.88	48	39.4	Irrev	0.428	−0.369	8.73			2 214
	−1.87	41		*d*										
(IX)	−0.70	60	3.14	Rev	+0.96	74	41.1	Rev	0.490	−0.309	10.91	10.69		2 214
	−1.20	90		Irrev										
(X)	−0.59	61	1.71	Rev	+1.52	37	29.1	Irrev	0.506	−0.303	9.35			2 223
	−1.12	79		Irrev										
(XI)	−1.86	38	2.44	*d*					0.741	−0.511		4.17 [k]		2 228
	−2.31	65		*d*										
(XII)	−2.09	51	2.20	*d*	+0.88	70	38.9	Irrev	0.466	−0.572		7.03 [k]		2 212
	−2.45	47		*d*										

[a] From a plot of E *vs.* log $[i/(i_{\mathrm{d}} - i)]$ (see text). [b] $I_{\mathrm{d}} = i_{\mathrm{d}}/Cm^{2/3}t^{1/6}$. Sample concentrations were 0.04—0.1mM. [c] At p.p.d.e. Sweep rate 0.5 V s^{-1}. rev = reversible; irrev = irreversible. [d] Beyond cathodic range of p.p.d.e. in AN. [e] From a plot of E *vs.* log $[(i_{\mathrm{L}} - i)/i]$. [f] At r.p.e. Units are μA/mmol radian$^{1/2}$ l^{-1} s$^{-1/2}$. [g] At p.p.d.e. Sweep rate 0.2 V s^{-1}. [h] Input parameters are as follows: ω — 1.4. Dimethylamino group: h_{N} 0.9, k_{CN} 1.0. Vinyl group C–C=C: $k_{\mathrm{C-C}}$ 0.9, $k_{\mathrm{C=C}}$ 1.1. Nitrile group C–C≡N: h_{N} 1.0, $k_{\mathrm{C \equiv N}}$ 1.5, $k_{\mathrm{C=C}} = 0.9$. For the julolidine and carbazole compounds a value of $k_{\mathrm{CN}} = 1.1$ was used. [i] From ref. 22, by the Halverstadt–Kumler method. [j] From ref. 23 for the dipropylamino-compound by the Halverstadt–Kumler method. [k] From A. L. McClellan, 'Tables of Experimental Dipole Moments' Freeman, San Francisco, 1963.

Values of $E_{1/2}$ for the first reduction wave in the present series range from −0.58 V *vs.* s.c.e. for *p*-nitrobenzylidenemalononitrile (V) to −2.09 V for *p*-dimethylaminocinnamonitrile (XII). The successive addition of cyano-groups to the vinyl double bond results in anodic shifts of *ca.* 0.7 V, as seen in the series (XII) ($E_{1/2}$ −2.09), (I) ($E_{1/2}$ −1.34), (IX) ($E_{1/2}$ −0.70). The shift is also seen between (XI) ($E_{1/2}$ −1.86) and (III) ($E_{1/2}$ −1.07) and between (VI) ($E_{1/2}$ −1.41) and (VII) ($E_{1/2}$ −0.72).

At the other end of the molecule, the replacement of a hydrogen atom on the benzene ring by a *p*-dimethylamino-group results in a cathodic shift of the first reduction wave of 0.2—0.3 V as seen with (XI) ($E_{1/2}$ −1.86) as compared to (XII) ($E_{1/2}$ −2.09) and with (III) ($E_{1/2}$ −1.07) as compared with (I) ($E_{1/2}$ −1.34). The effect of substituent on reduction potential is most clearly

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[14] J. E. Kuder, D. Wychick, R. L. Miller, and M. S. Walker, *J. Phys. Chem.*, 1974, **78**, 1714.

[15] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[16] M. E. Peover, *Trans. Faraday Soc.*, 1964, **60**, 417.

seen with compounds (I)—(V) where the trend is described by the Hammett–Zuman [17,18] relationship (1) (correlation coefficient, *r* 0.990).

$$E_{1/2,\mathrm{X}} - E_{1/2,\mathrm{H}} = 0.37\sigma- \qquad (1)$$

Compound (V) deserves special comment, since the nitro-group is itself electroactive and, in related series of substituted compounds, is frequently reduced at potentials less negative than expected from a $\rho\sigma_{\mathrm{X}}$ plot for the series as a whole.[17] That the dicyanovinyl group is the electrophore involved in the first reduction wave is supported by the agreement of the log plot analysis and c.v. response with the other members of the series.

The third reduction wave of (V), which has a log plot slope of 60 mV and shows reversible c.v. behaviour, has a half-wave potential (−1.14 V *vs.* s.c.e.) essentially the same as that reported for the reversible one-electron reduction of nitrobenzene in AN(−1.15 V),[19] and is probably associated with the nitro-group as the electroactive moiety.

Finally, the effect of increasing the separation between the donor and acceptor ends of the molecule is seen in the comparison of $E_{1/2}$ for (I) (−1.34 V) with that of (VIII) (−1.11 V). The anodic shift of 0.2 V in half-wave potential caused by the insertion of an ethylene unit is thus relatively small.

The results of oxidation studies on compounds (I) (XII) using an r.p.d.e. are summarized in Table 1. Oxidation waves were observed only for the compounds containing amino-nitrogen atoms *para* to the acceptor end of the molecule. Compounds (I), (VI), (VII), and (IX) show reversible c.v. behaviour with a separation of 0.07—0.08 V between anodic and cathodic peaks, independent of sweep rate and consistent with a reversible one-electron process. Since the value of the current function $i_{\mathrm{L}}/C\omega^{1/2}$ is fairly constant throughout the series (i_{L} is the limiting current, C the concentration, and ω the rotation speed of platinum disc), it may be assumed that the irreversible oxidations also correspond to one-electron processes. In contrast to the reduction behaviour, there is no single structural feature which distinguishes the compounds on the basis of reversibility of the oxidation step.

The half-wave potentials of those compounds undergoing oxidation cover a smaller range (+0.9 to +1.1 V) than do their reduction potentials, with the exception of the tricyanovinylcarbazole compound (X) ($E_{1/2}$ + 1.52 V). The log plot slope obtained for (X) is also somewhat lower than that observed for the other compounds. This difference may be explained if one assumes that in the oxidation step an electron is removed from an orbital essentially localized on the amino-nitrogen with minor perturbations from the rest of the molecule. In the case of (X) the nitrogen lone pair electrons are delocalized over the carbazole nucleus and thus are less easily removed. The greater delocalization of the nitrogen lone pair electrons in carbazole is also reflected in the lower basicity of carbazole (pK_{a} *ca.* −60) [20] relative to that of diphenylamine (pK_{a} 0.78).[21]

Dipole Moments.—The dipole moments obtained for the compounds in the present study are given in Table 1, and range from 3.05 D for *p*-nitrobenzylidenemalononitrile (V) to 10.9 D for *p*-(tricyanovinyl)-*NN*-dimethylaniline (IX). For those members of the present series whose dipole moments have been reported,[22,23] there is good agreement with the results of this work. The values for the benzylidenemalonitriles (I)—(V), may be correlated by means of the Hammett substituent constant [18] as described by the least squares regression line (2) (*r* −0.987).

$$\mu = -3.57\sigma_{\mathrm{p}} + 5.42 \qquad (2)$$

It should, in principle, be possible to estimate how much of the observed dipole moment is due to intramolecular donor–acceptor interaction.[24a] If little interaction occurs between substituents, the dipole moment of a disubstituted benzene may be calculated by simple vector addition.[24b] For this purpose the magnitude of the dicyanovinyl group moment is taken to be equal to the dipole moment of (III) (5.24 D) and a value of 120° chosen as not unreasonable for the angle which the dicyanovinyl group moment makes with the bond connecting it to the benzene ring. The group moments and angles for the substituents $(CH_3)_2N$, CH_3O, Cl, and NO_2 can be taken from the literature [25b] and used to calculate dipole moments for compounds (I)—(V) assuming no interaction between substituents. These values are given in Table 1.

The difference between the observed dipole moments and those calculated by vector addition, $\mu_{\mathrm{exp}} - \mu_{\mathrm{calc}}$, may be considered as that portion of the dipole moment which is due to resonance interaction between the substituents. This difference has been termed the interaction moment [25] μ_{int}, and may be related to the Hammett substituent constant, the relation for the present case being described by the regression line (3) (*r* −0.991).

$$(\mu_{\mathrm{exp}} - \mu_{\mathrm{calc}}) = 2.65\sigma_{\mathrm{p}} + 0.18 \qquad (3)$$

Such correlations between dipole moment or interaction moment and substituent constant may be discussed in terms of relative contributions of resonance hybrids to the ground state structures. Thus, in passing from electron-withdrawing to electron-releasing sub-

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[17] P. Zuman, ' Substituent Effects in Organic Polarography,' Plenum Press, New York, 1967.

[18] Values for the substituent constants are taken from C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, 1964, **2**, 323.

[19] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, 1960, **33**, 825; *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

[20] H. J. Chen, L. E. Hakka, R. L. Hinman, A. J. Kresge, and E. B. Whipple, *J. Amer. Chem. Soc.*, 1971, **93**, 5102.

[21] D. Dolman and R. Steward, *Canad. J. Chem.*, 1967, **45**, 904.

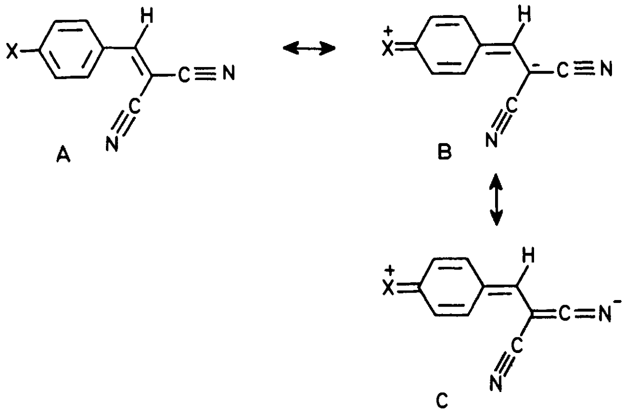
[22] H. Weiler-Feilchenfeld, I. Agranat, and E. D. Bergman, *Trans. Faraday Soc.*, 1966, **62**, 2084.

[23] I. Agranat, Z. Rappoport, and H. Weiler-Feilchenfeld, *Trans. Faraday Soc.*, 1970, **66**, 769.

[24] V. I. Minkin, O. A. Osipov, and Y. A. Zhdanov, ' Dipole Moments in Organic Chemistry,' Plenum Press, New York, 1970, (*a*) ch. 5; (*b*) ch. 3.

[25] R. J. K. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 599, 1383.

stituents, the dipole moment reflects increasing contributions from resonance structures B and C.



We may consider 9-dicyanovinyljulolidine (VI) to be an additional member of the substituent series just discussed. Its dipole moment, 9.43 D, reveals the julolidine grouping to be very strongly electron releasing as compared to that of the dimethylamino-group as seen in (I) (μ 8.70 D).

9-Tricyanovinyljulolidine (VII), which is related to (VI) by the addition of a third cyano-group to the vinyl moiety, is found to have a dipole moment of 10.23 D, *i.e.*, the additional cyano-group results in an increase of 0.8 D in dipole moment. By comparison, the dipole moment of *p*-tricyanovinyl-*NN*-dimethylaniline (IX), is 10.91 D, *i.e.* 2.2 D greater than that of the corresponding dicyanovinyl compound (I). Surprisingly, the dipole moment of (VII) is 0.7 D less than that observed for (IX).

In *p*-dimethylaminocinnamylidenemalononitrile (VIII), the acceptor end of the molecule is separated from the donor end by an additional ethylene unit relative to (I), yet its dipole moment (8.73 D) is <0.1 D greater than that of (I).

This result suggests that the net dipole moment may be represented as the sum of the group moments essentially localized on the dimethylamino and dicyanovinyl groups, thus independent of their separation, although dependent on the angle between the substituents. By comparison, the observed dipole moment of cinnamonitrile (4.17 D) [26] is only 0.1 D greater than that of benzonitrile (4.05 D).[27]

The last compound studied, 3-tricyanovinyl-*N*-ethylcarbazole (X), incorporates a nitrogen atom with its lone pair of electrons within an aromatic ring system. Presumably the nitrogen atom is coplanar with the benzenoid rings of the molecule yet its observed dipole moment (9.35 D) is less than that of the other two tricyanovinyl compounds (VII) and (IX). This lower tendency for the carbazole group to act as an electron donor moiety with respect to the tricyanovinyl group is in agreement with the higher oxidation potential observed for (X).

I.r. Spectra.—The information regarding ground state charge distribution obtained from the dipole moment measurements is supplemented by i.r. absorption data of the compounds. The nitrile stretching frequencies were readily identified and these are given in Table 1. Interestingly, for both the dicyanovinyl and tricyanovinyl compounds only a single C≡N stretching band was seen.

For compounds (I)—(V), the trend is readily accommodated by use of Hammett substituent constants. As implied by resonance structures B and C, an increased dipole moment due to conjugative interaction between the two substituents should be accompanied by a lowering of the nitrile bond order. This in turn should be seen as a decreased stretching frequency of the cyano-group in the i.r. spectrum. This expected trend is indeed seen and may be represented by the least squares line (4) (r + 0.988).

$$\bar{\nu}_{CN} = 13.0\sigma_p + 2\,226 \qquad (4)$$

The correlation is not readily extended to the rest of the series, but a correlation between molecular dipole moment and nitrile stretching frequency might be expected. When a plot of $\bar{\nu}_{CN}$ against μ is made (Figure 3), it is seen that this expectation is indeed borne out.

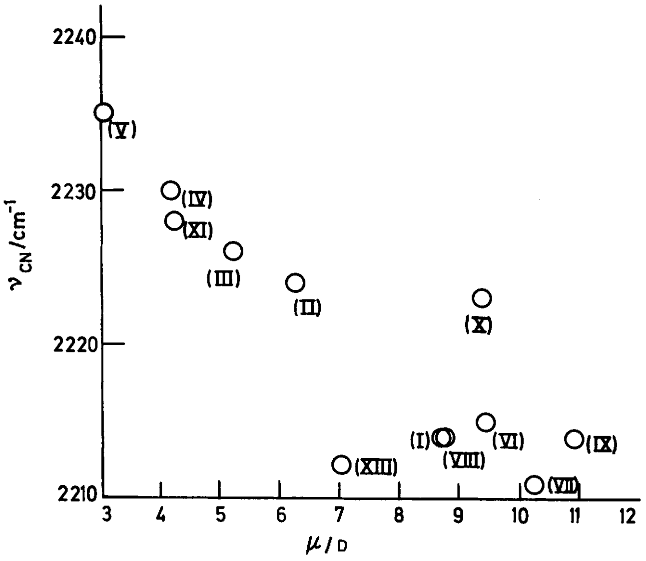


FIGURE 3 Plot of nitrile stretching frequency *vs.* molecular dipole moment for compounds (I)—(XII)

The tricyanovinylcarbazole compound (X) seems to be an exception.

^{1}H *N.m.r. Spectra.*—Analogous evidence for the strong interaction between donor and acceptor ends of the molecule may be seen in the ^{1}H n.m.r. spectra of compounds (I)—(V). This is seen in Figure 4, where the chemical shift of the vinyl proton of the dicyanovinyl group is plotted against the Hammett constant of the *para*-substituent (slope 0.46, r +0.936). This may be

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[26] H. L. Goebel and H. H. Wenzke, *J. Amer. Chem. Soc.*, 1937, **59**, 2301.

[27] K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 1951, 2807; C. W. N. Cumper and A. I. Vogel, *ibid.*, 1960, 4723.

contrasted with the considerably smaller substituent dependence of the chemical shift of methyl protons in substituted toluenes[28] (Figure 4, slope 0.17). Although both sets of data are for protons on a carbon atom α to an aromatic ring, in the case of the *para*-substituted toluenes resonance interactions are restricted to the benzene nucleus, while in the benzylidenemalononitriles such effects are transmitted along a conjugated chain to a strong electron-withdrawing group of which the proton bearing carbon atom is a part.

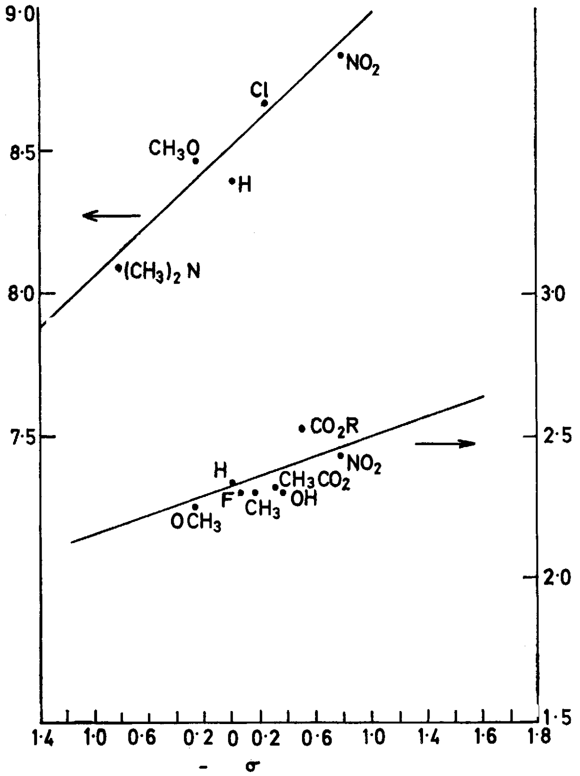

FIGURE 4 Chemical shift *vs.* Hammett substituent constant. Top: methine proton of benzylidenemalononitriles (I)—(V). Bottom: methyl protons of *p*-substituted toluenes

Not unexpectedly the chemical shifts of the ring protons of compounds (I)—(V) also reflect the changes of electron density caused by differing substituents *para* to the dicyanovinyl moiety. As shown in Figure 5, the chemical shift of the protons *ortho* to the donor substituent exhibit a greater dependence on changes in that substituent than do the *meta* protons. The result is that the two correlation lines approach one another as the varied substituent becomes more electron withdrawing and thus more like the dicyanovinyl group.

Julolidine Substituent Constant.—The julolidine compounds (VI) and (VII) may be considered as di- and tricyanovinylbenzenes substituted by a *para*-dialkylamino-group and twice by *meta*-alkyl groups. The substituent effect of the entire $N(C_3H_6)_2$ moiety may be estimated from the Hammett correlation lines for compounds (I)—(V) and an effective substituent assigned to this group. The largest effect is seen in the chemical shift of vinyl proton which reflects the electron density at this position and from the correlation line shown in Figure 4 a value of σ of -1.7 can be estimated. The smallest effect is seen in the i.r. data, reflecting nitrile bond order, which leads to σ -0.85. Estimates from other data obtained in this study fall between these extremes: ring proton chemical shift (Figure 5), σ -1.4; dipole moment [equation (2)], σ -1.1; reduction potential [equation (1)], σ -0.92. While it would be presumptuous to assign a ' best ' σ constant from this range of values, the overall picture which emerges is quite clear. The electron-releasing ability seen in the julolidine compounds is greater than simply the additive contributions of p-$(CH_3)_2N$ plus two *meta*-alkyl substituents. This enhanced effect must be due to steric constraints which favour coplanarity of the nitrogen atom with the benzene ring and thus increase conjugative interaction with the electron-withdrawing dicyanovinyl moiety.

MO Calculations.—An attempt was made to give a unifying framework to some of the structural correlations described above. For this purpose the HMO-ω technique[29] was used with heteroatom parameters based on those given by Kier[30] and Tollenaere.[31] Calculations were not performed for compounds (II), (IV), and (V) since it was not thought worthwhile to optimize the additional parameters required for the CH_3O, Cl, and NO_2 substituents.

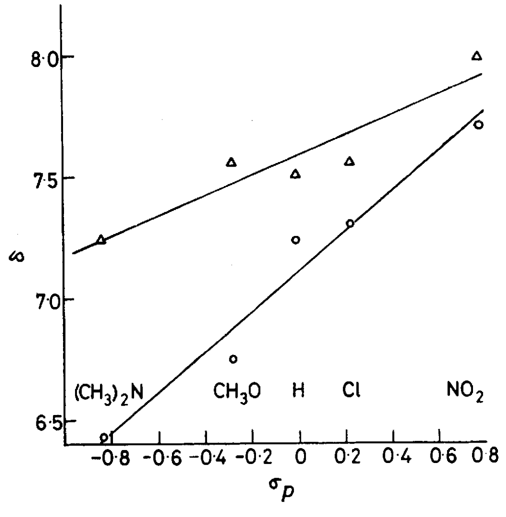

FIGURE 5 Chemical shift *vs.* Hammett substituent constant for compounds (I)—(V). ○ ring protons *ortho* to donor substituent; △ ring protons *ortho* to dicyanovinyl group

The results of the HMO-ω calculation are given in Table 1. The relation between half-wave reduction potential and the energy of the lowest unoccupied

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[28] L. M. Jackman, 'Applications of Nuclear Magnetic Resonance Spectroscopy,' Pergamon, London, 1959, p. 58.

[29] A. Streitwieser, jun., ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, ch. 4.

[30] L. B. Kier, *Tetrahedron Letters*, 1965, 3273.

[31] J. P. Tollenaere, *Tetrahedron Letters*, 1972, 2275.

molecular orbital, E_{LUMO}, is described by the least-squares equation (5) (r 0.988). That the second electron

$$E_{1/2}(\mathrm{red}) = 5.36E_{\mathrm{LUMO}} + 0.99 \qquad (5)$$

enters the same virtual orbital as the first is indicated by the observation that the second reduction potentials also vary with E_{LUMO}, as described by the correlation equation (6) (r 0.962). These correlations include

$$E_{1/2}\ (\mathrm{red}) = 4.87E_{\mathrm{LUMO}} + 0.24 \qquad (6)$$

within a single framework the previously discussed shifts in $E_{1/2}$ caused by the number of nitrile groups attached to the vinyl double bond, amino-substitution *para* to the acceptor group, and increased separation between the donor and acceptor ends of the molecule. The observed correlation is especially gratifying when it is noted that both reversible and irreversible reductions are included in the same plot.

The energies of the highest occupied molecular orbitals, E_{HOMO}, in the compounds for which oxidation waves were observed are calculated to be rather similar, in agreement with experiment. The observation that it is somewhat more difficult to remove an electron from the carbazole compound (X) is as might be expected from comparison of calculated values of E_{HOMO}. Further examination of Table 1 shows that oxidation of compounds (III) and (XI) should be even more difficult, and in fact these compounds showed no oxidation waves in the experimentally accessible range.

Relation between Reduction Potential and Dipole Moment.—The effect of changing substituents on the benzene ring is such that as the substituent becomes more electron releasing, the dipole moment becomes greater and the reduction potential becomes more negative. A recently proposed empirical relationship by Gorokhovskaya [32] describes this trend by equation (7)

$$\log|E_{1/2}| = k/(\mu - \mu_{s}) - a \qquad (7)$$

where μ_s is the dipole moment of the solvent and k and a are constants arising from the least squares treatment of the data. This equation appears to have no theoretical foundation, and in fact a simple linear correlation is to be preferred. For compounds (I)—(VI) the correlation is given by (8) (r —0.933). The mono- and tri-

$$\mu = -7.82\ E_{1/2} - 2.44 \qquad (8)$$

cyanovinyl compounds fall on either side of this correlation line. That a linear correlation between μ and $E_{1/2}$ should exist is, of course, implied by the Hammett relationships that exist for both, but may also be argued as follows. It has been shown [33] that the effect of a substituent may be treated as a change in the Coulomb integral of the atom to which the substituent is attached. Now, from the perturbational MO approach [34] changes in both MO energy levels (hence $E_{1/2}$) and charge densities at each atom (hence dipole moment) are linearly related to changes in the Coulomb integral of a given atom. Thus, $E_{1/2}$ and μ should be linearly related to each other as long as we are dealing with perturbations to the same molecular framework. Similar arguments apply changes in bond order and hence i.r. stretching frequencies.

Relation to Electrical Properties.—We return now to the question raised in the introduction, namely the relationship between molecular electronic structure and the electrical behaviour of the compounds in the solid. Several of the compounds reported in this paper have recently been examined in these laboratories [35] by the xerographic discharge technique.[36] In this method, films composed of 5 wt. % of the compound in poly-(N-vinylcarbazole) binder are cast on a conductive substrate. The surface of the film is charged with a corona device and then exposed to a pulse of light corresponding to the absorption maximum while the surface potential is monitored. The initial discharge rate $(\mathrm{d}V/\mathrm{d}t)_0/d$ (where d is the film thickness) should correspond to the quantum yield for charge carrier generation.[35]

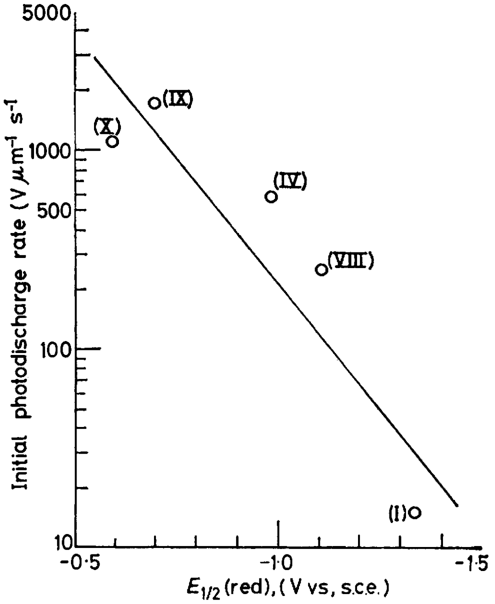

FIGURE 6 Initial photodischarge rate for compounds in poly(vinylcarbazole) matrix against their solution reduction potentials

In Figure 6 is shown the relationship between initial photodischarge rates and reduction potential of the compound. Although the details of the mechanism are not established, the correlation may be rationalized if one assumes that the charge carrier generation step involves

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[32] A. S. Gorokhovskaya, *Elecktrokhimiya*, 1970, **6**, 1122; 1972, **8**, 644.

[33] Y. M. Krygowski and P. Tomasik, *Bull. Acad. Pol. Sci., Ser. Sci. Chem.*, 1970, **18**, 303.

[34] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1947, **A191**, 39.

[35] W. W. Limburg, J. M. Pearson, and D. J. Williams, to be published.

[36] P. J. Regensberger, *Photochem. Photobiol.*, 1968, **8**, 429.

a transfer of an electron from carbazole moieties of the matrix to the guest molecules in the matrix. The efficiency of the process then becomes greater as the tendency of the acceptor molecule to gain an electron increases. This tendency, of course, may be directly obtained from the solution reduction potential of the acceptor molecule.

It is understood that experimental photodischarge measurements may reflect other factors than simply the energy levels of the guest molecule. Further studies are necessary to clarify the influence of excited state dipole moments, matching of energy levels between the guest compounds and those of the binder matrix, and of transport efficiencies. The exact mathematical modelling of the relationship between molecular energy levels and photodischarge rates would be extremely useful. As implied from the earlier discussion these studies may be supported by molecular orbital and linear free energy relationships. Nonetheless, the results of the present study demonstrate the utility of solution redox data and point the way for further studies.

EXPERIMENTAL

Materials.— *p*-Dimethylaminobenzylidenemalononitrile (I) was prepared by the condensation of equimolar amounts of *p*-dimethylaminobenzaldehyde and malononitrile in refluxing tetrahydrofuran (THF) in the presence of glacial acetic acid and ammonium acetate. The orange crystalline product (30.5%), after crystallization from glacial acetic acid, washing with cold ethanol, and drying in a vacuum desiccator, had m.p. 179—181° (lit.,[37] 179—180°). *p*-Methoxybenzylidenemalononitrile (II), obtained from Aldrich Chemical Co., after two crystallizations from acetic acid had m.p. 111—113° (lit.,[38] 114.5—115°). Condensation of benzaldehyde and malononitrile afforded benzylidenemalononitrile (III) in 41% yield, which after crystallization once from ethanol and twice from hexane–ethanol (95 : 5) had m.p. 83° (lit.,[38] 83.5—84°). *p*-Chlorobenzylidenemalononitrile (IV) was obtained by the condensation of *p*-chlorobenzaldehyde and malononitrile. After two crystallizations from ethanol the product (8.5%) had m.p. 158° (lit.[39] 162—163°). *p*-Nitrobenzylidenemalononitrile (V) obtained from Aldrich Chemical Co., was recrystallized twice from ethanol, m.p. 159—160° (lit.,[39] 158°).

9-*Dicyanovinyljulolidine* (VI). The reaction of dimethylformamide and phosphoryl chloride with julolidine resulted in the formation of julolidine-9-carbaldehyde, m.p. 77—79°, in 68% yield. Condensation of the latter with malononitrile afforded the desired product (33%), which after recrystallization from methanol had m.p. 159—161° (lit.,[40] 163—165°).

9-*Tricyanovinyljulolidine* (VII). This compound was prepared in 26% yield, by the reaction of julolidine with tetracyanoethylene. The product after recrystallization from cyclohexanebenzene had m.p. 265° (lit.,[40] 265—266°).

p-NN-*Dimethylaminocinnamylidenemalononitrile* (VIII). A mixture of malononitrile (3.30 g, 0.05 mol), 4-dimethylaminocinnamaldehyde (8.76 g, 0.05 mol), glacial acetic acid (1.0 ml), ammonium acetate (0.35 g), and THF (50 ml) was heated to reflux temperature for 5 h. When the

TABLE 2

Dielectric constant and refractive index data

Compound	10^6 Concentration (mol ml^{-1})	Dielectric constant	Refractive index
(I)	1.23	2.288 2	1.498 052
	2.10	2.296 7	1.498 158
	4.10	2.316 1	1.498 350
	6.00	2.334 6	1.498 254
S 515.5 ± 3.7			
μ 8.70 ± 0.06			
(II)	2.69	2.291 5	1.497 860
	5.13	2.304 4	1.497 956
	10.2	2.330 8	1.498 350
	11.2	2.335 1	1.498 300
S 267.1 ± 3.0			
μ 6.26 ± 0.07			
(III)	3.78	2.290 1	1.498 097
	5.54	2.296 2	1.498 097
	7.56	2.303 3	1.498 097
	11.7	2.318 2	1.498 097
S 187.3 ± 1.5	18.6	2.341 7	1.498 097
μ 5.24 ± 0.04			
(IV)	1.36	2.277 6	1.497 908
	2.54	2.280 3	1.497 956
	5.02	2.285 4	1.498 029
	7.11	2.290 7	1.498 110
	10.1	2.297 5	1.498 158
S 119.1 ± 2.2			
μ 4.18 ± 0.08			
(V)	1.17	2.276 2	1.497 908
	2.21	2.278 2	1.498 004
	3.80	2.279 9	1.498 050
	6.66	2.283 8	1.498 158
	11.4	2.289 5	1.498 302
S 63.46 ± 1.62			
μ 3.05 ± 0.08			
(VI)	0.094 3	2.275 7	1.497 908
	0.474	2.280 2	1.498 004
	2.36	2.303 9	1.498 158
	3.41	2.314 9	1.498 206
	5.89	2.3418	1.498 302
S 606 ± 14			
μ 9.43 ± 0.22			
(VII)	0.129	2.282 3	1.497 908
	0.336	2.285 0	1.498 206
	0.853	2.292 0	1.498 302
	1.56	2.302 2	1.498 302
S 713 ± 29			
μ 10.23 ± 0.42			
(VIII)	0.297	2.281 8	1.497 812
	1.58	2.295 5	1.498 206
	2.71	2.306 4	1.498 302
S 519 ± 6			
μ 8.73 ± 0.11			
(IX)	0.214	2.279 9	1.497 908
	1.17	2.288 6	1.498 110
	1.86	2.303 5	1.498 254
S 811 ± 66			
μ 10.91 ± 0.89			
(X)	0.952	2.282 9	1.497 956
	2.08	2.294 2	1.497 956
	2.96	2.305 6	1.498 004
	3.56	2.312 1	1.498 302
S 595 ± 22			
μ 9.35 ± 0.36			

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[37] R. Legrand, *Bull. Soc. chim. belges*, 1944, **53**, 166.

[38] B. B. Corson and R. W. Stoughton, *J. Amer. Chem. Soc.*, 1928, **50**, 2825.

[39] H. G. Sturz and C. R. Noller, *J. Amer. Chem. Soc.*, 1949, **71**, 2949.

[40] B. C. McKusick, R. Heikert, T. L. Carins, D. Coffman, and H. Mower, *J. Amer. Chem. Soc.*, 1959, **80**, 2086.

dark brown solution was cooled a grey product precipitated. This material (6.8 g, 34.0%) was recrystallized from cyclohexane–benzene, m.p. 146—147° (Found: C, 74.5; H, 5.75; N, 18.55. $C_{14}H_{13}N_5$ requires C, 75.3; H, 5.75; N, 18.8%).. This product possessed solvatochromic as well as thermochromic properties.

4-*Tricyanovinyl*-NN-*dimethylaniline* (IX). This compound was prepared in 30% yield according to the method of McKusick and Melby,[41] m.p. 174—176° (lit.,[41] 173—175°).

N-*Ethyl*-3-*tricyanovinylcarbazole* (X). *N*-Ethylcarbazole (1.0 g, 5.2×10^{-3} mol) in DMF (20 ml) was placed in a 50 ml one-necked flask equipped with a magnetic stirring bar and nitrogen blanket. As soon as tetracyanoethylene (0.67 g, 5.2×10^{-3} mol) was added, the solution turned blue. This mixture was heated at 100° for 20 h. While still hot, the solution was poured into water (60 ml). Red-brown crystals were isolated and washed several times with ethanol. The brick-red crystals (1.13 g, 73%) remaining after washing with ethanol had m.p. 239—241° (Found: C, 77.25; H, 4.05; N, 18.8. $C_{19}H_{12}N_4$ requires C, 77.0; H, 4.1; N, 18.9%).

Cinnamonitrile (XI) (Aldrich) was used as received.

p-Dimethylaminocinnamonitrile (XII) (Aldrich) was crystallized from ethanol prior to use.

For the electrochemical measurements, acetonitrile (AN) (Burdick and Jackson) was distilled from Na_2CO_3 and $KMnO_4$, then acidified and fractionally distilled.[42] The water content after this treatment was *ca.* 1mM by Karl Fischer titration. The supporting electrolyte for the electrochemical measurements was tetraethylammonium perchlorate (TEAP) from Southwestern Analytical Chemicals, dried for 16 h under vacuum.

Measurements.—Electrochemical measurements were made using a PAR 170 electrochemistry system in the three-electrode mode. For reductions a dropping mercury electrode (d.m.e.) was used, with the following capillary characteristics: m 1.65 mg s^{-1}, t 4.10 s measured with an open circuit at h 79 cm. A Beckman rotating electrode (rotation speed 1 800 r.p.m.) with a planar platinum tip of area 0.30 cm^2 was used to study oxidations. For cyclic voltammetry a planar platinum disc with electrode area 0.22 cm^2 was used. The reference electrode was a saturated calomel electrode (s.c.e.) in which the KCl solution was replaced by saturated aqueous NaCl. This change eliminates electronic noise at low sample concentration due to precipitated $KClO_4$ at the tip of the reference electrode. Potentials determined with respect to this modified electrode are related to the conventional s.c.e. by the conversion $E(\mathrm{KCl}) = E(\mathrm{NaCl}) - 0.01$ V and are so reported. The auxiliary electrode was a platinum wire spatial for d.c. voltammetry and a platinum disc for cyclic voltammetry.

Voltammetric measurements were made with sample concentrations of $1-5 \times 10^{-4}$M with 0.1M-TEAP as supporting electrolyte. No change was seen in the polarogram of a sample left overnight; however, determinations were usually made within 1 h of sample preparation after a 10 min purge with purified nitrogen.

Controlled potential electrolysis of benzylidenemalononitrile (III) was performed using a three-compartment cell with a mercury pool as the working electrode. Sample concentration was 3×10^{-3}M with the applied potential corresponding to the start of the plateau of the first polarographic reduction wave. The reduction product, after evaporation of solvent and extraction of the residue with ether, was a brown oil containing three components (t.l.c. on silica gel). The presence of two i.r. absorption bands (2 190 and 2 170 cm^{-1}) seen in the region corresponding to the nitrile stretching frequency indicated that the nitrile function was not the site of reduction.

Dielectric and refractive index measurements were performed using reagent grade benzene (Baker) that had been washed in succession with concentrated H_2SO_4, water, aqueous Na_2CO_3, and water, then dried over 5A molecular sieves, distilled, and stored in dark bottles over sodium.

Solution dielectric measurements (three terminal method) were performed with a General Radio 1615-A capacitance bridge at frequencies of 1 and 10 KHz and, within the limits of experimental error, were constant for all solution concentrations. A constant temperature stainless steel cell through which regulated water from a Haake constant temperature bath circulated was designed for the experiments. The cell was repeatedly filled with fresh solution (at a given concentration) until three consecutive sets of data differing by less than one part in 10^4 were obtained. The dielectric constant (ε) of the solutions was measured by the substitution technique with an air reference. The cell gap was set by a Teflon^R spacer. A one inch diameter electrode was used in all experiments.

Refractive indices (n) were measured with a Bausch and Lomb precision refractometer at 25.00 ± 0.02 °C. To obtain the molecular dipole moment the data were treated by the Guggenheim method[43] in which the quantity $(\varepsilon - n^2)/(\varepsilon + 2)(n^2 + 2)$ is plotted against concentration. The slope (S) of the best straight line then affords the dipole moment by the relation $\mu = (S \cdot 27\boldsymbol{k}T/4\pi N)^{1/2}$ where $\boldsymbol{k} =$ Boltzmann's constant and $N =$ Avogadro's number. Plots of ε and n^2 against concentration were linear so that association does not occur in the range considered. The results are summarized in Table 2.

I.r. spectra were taken as Nujol mulls on a Beckman IR 12 instrument, scanning the range 1 900—2 300 cm^{-1} at 20 cm^{-1} min^{-1}. N.m.r. spectra were obtained using a JEOL C-60H instrument, with samples at 10% w/v in [$^2H_6$]DMSO with tetramethylsilane as internal standard.

We thank Drs. J. M. Pearson and D. J. Williams for permission to quote results of their studies prior to publication and Dr. P. Zuman for useful discussions.

[6/1955 *Received*, 19*th October*, 1976]

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[41] B. C. McKusick and L. R. Melby, *Org. Synth.*, 1963, **4**, 953.

[42] J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Analyt. Chem.*, 1965, **37**, 1161.

[43] E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.