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SPECTRAL AND THERMAL CONDUCTANCE STUDIES OF SOME SYMMETRIC 1,5-DIPHENYL-3-CYANOFORMAZANS. SCF PPP CI CALCULATION

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ABSTRACT

Various cyanoformazans were prepared and subjected to elemental analysis and melting point measurements. UV and IR spectral behaviours were studied and the results were correlated with those obtained from a theoretical treatment applying the self-consistent field approach of Pariser, Parr and Pople. The electrical conductance was studied and the activation energies were determined and correlated with the theoretical data.

INTRODUCTION

Formazans are those compounds which contain the chain of atoms –N=N–C=N–NH–. They exhibit distinct and characteristic properties. Yurchenko et al. [1] studied the UV spectra of some substituted formazans and their nickel complexes in different solvents. Spectroscopic studies of 3-carboxymethylthio-1,5-diphenylformazan have demonstrated the presence of *anti, s-trans, syn* and *s-cis* isomers in solution [2]. IR studies of some formazan derivatives have led to the conclusion that the heterocyclic system has an asymmetric distribution of electron density [3]. Mester et al. [4] studied the NMR spectra of several sugar and non-sugar formazans. There have been numerous investigations of the suitability of various formazans and their metal complexes for use as dyes [5,6]. The symmetric 1,5-diphenyl-3-cyanoformazan and its derivatives have been used as analytical reagents for determining various metals [7,8].

The present work was undertaken essentially to study the spectral behaviour, solvent effect and electrical conductivity of some symmetric 1,5-di-

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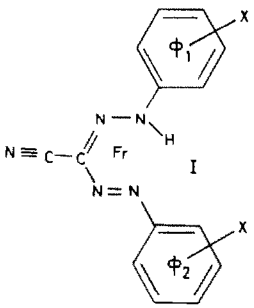
phenyl-3-cyanoformazans. An attempt was made to correlate the experimental results with those obtained theoretically using the self-consistent field approach due to Pariser and Parr [9] and Pople [10] with configuration interaction (SCF PPP CI).

The 1,5-bis-diphenyl-3-cyanoformazans under investigation Ia–g are given below:



X=H(Ia), p-CH_3(Ib), p-OCH_3(Ic), p-Cl (Id),
p-Br (Ie), p-I (If) and o-COOH (Ig)

Scheme 1.

EXPERIMENTAL

The chemicals used in this investigation were of the highest purity. The solvents used, cyclohexane, acetone, dioxane, isopropanol and chloroform, were purified by the recommended method [11]. Water was always twice distilled.

The symmetric formazans were prepared by coupling the corresponding diazonium chloride with ethylcyanoacetate in the molar ratio 2:1 in an alkaline medium (sodium hydroxide). The resulting crude products were crystallized out using a suitable solvent. The symmetric cyanoformazans thus formed were subjected to elemental analysis and melting point measurements. The results were in good agreement with the theoretical values; the melting points were consistent with those previously reported [12–16]. Analytical data are given below as substituent, experimental (literature) melting point: H, 155 (158); *p*-CH_3, 222 (217); *p*-OCH_3, 184 (180); *p*-Cl, 245 (240); *p*-Br, 263 (260); *p*-I, 276 (–); *o*-COOH, 225 (225).

The electronic absorption spectra of the formazans under investigation in different organic solvents were obtained using a PYE UNICAM SP 1750 recording spectrophotometer.

The IR spectra were recorded in the form of KBr pellets using a Pye Unicam SP 3-300 infrared spectrophotometer.

For electrical measurements the prepared samples were pressed into pellets at a pressure of about 600 kg cm^{-2} at which the electrical conductivity was independent of load [17]. The specimen was fixed to the double electrode by silver paste. The sample holder with specimen was placed inside a vertical tube which incorporated windings running in opposite directions to eliminate fields caused by the heating current. The $I-V$ characteristics of the set-up were analysed and showed a linear relationship proving the ohmic nature of the contacts. Moreover, after the voltage was applied, no time dependence of the electrical resistance was observed, indicating that the ionic contribution to conductance was negligible.

The d.c. measurements were made using a stabilized d.c. power supply BS 275 and a Leybold model 532-01 measuring current amplifier. The e.m.f. of a thermocouple (0.1 mm chromel–alumel wires), measured using a digital multimeter PM 2421,was used to record the temperature of the sample. Measurements were taken every 3° C over the working range.

METHOD AND PARAMETERS

The method used is well known and has been described elsewhere [18], using the self-consistent field approach due to Pariser and Parr [9] and Pople [10]. All carbon–carbon grid distances were assumed to be 1.399 Å, bond angles 120°, valence state ionization potential α 11.16 eV, core integral β 2.379 eV, and one-centre electron repulsion integrals γ 11.350 eV. Modifications were made when necessary for the heteroatoms, as indicated in Table 1, and for singlet excited configurations in the CI matrix.

Calculations were carried out using Cairo University ICL 2957/VME computing system.

TABLE 1

Parameters used for PPP CI calculations [19,20]

$\alpha_{O.} = -06.540$	$\gamma_{O.} = 15.230$	$\beta_{CO.} = 02.379$
$\alpha_{O:} = -16.010$	$\gamma_{O:} = 21.530$	$\beta_{CO:} = 01.900$
$\alpha_{N.} = -02.940$	$\gamma_{N.} = 12.340$	$\beta_{CN.} = 01.900$
$\alpha_{N:} = -11.970$	$\gamma_{N:} = 17.440$	$\beta_{CN:} = 02.770$
$\alpha_{\ddot{O}(Me)} = -17.740$	$\gamma_{Cl:} = 13.030$	$\beta_{CCl:} = 01.900$
$\alpha_{Cl:} = -15.200$	$\beta_{Br:} = 12.190$	$\beta_{CBr:} = 01.650$
$\alpha_{Br:} = -13.100$	$\gamma_{I:} = 11.000$	$\beta_{CI:} = 01.400$
$\alpha_{I:} = -10.670$		

Dots indicate whether the atom contributes one or two electrons to the π system.

RESULTS AND DISCUSSION

Electronic absorption spectra

The electronic absorption spectra of the formazans in organic solvents of different polarities (ethanol, isopropanol, acetone, chloroform, dioxane and cyclohexane) were obtained. Those for ethanol and dioxane are shown in Fig. 1. The spectra in ethanol and cyclohexane display mainly four bands. The first band at 210–235 nm may be assigned to a π–π^* transition within the phenyl moieties (^1L_a–1_A). This band disappeared in the other solvents. The second band at 245–290 nm may be assigned to the low energy π–π^* transition (^1L_b–1_A) within the benzene ring. A third band, within the 286–324 nm range, may be attributed to π–π^* electronic transition within the hydrogen ring formed between azo and hydrazo groups. The fourth band, located at 416–490 nm in the visible region, is assigned to a π–π^* transition within the azo group N=N [21]. It may be influenced by an intramolecular charge transfer since its position is affected by varying the solvent.

Solvent effect on absorption bands

In order to verify the solvent effect on the band shift, the relation of Gati and Szalay [22] was applied in the form

$$\Delta\bar{\nu} = (a - b)\frac{n^2 - 1}{2n^2 + 1} + b\frac{D - 1}{D + 1}$$

where n is the refractive index of solvent, D is the dielectric constant of solvent, and a and b are constants.

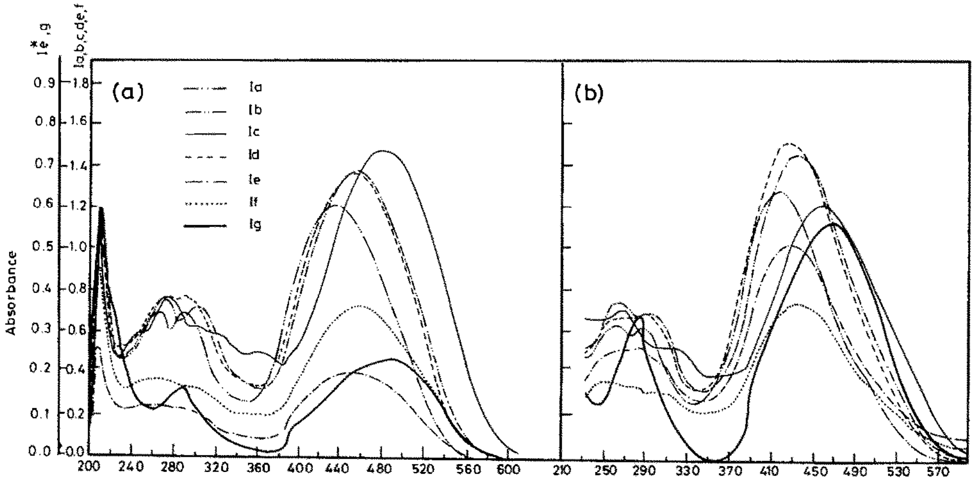


Fig. 1. Electronic absorption spectra of 0.5×10^{-4} M Ia–g dissolved in (a) ethanol and (b) dioxane.

TABLE 2

Calculated and observed transition energies E, oscillator strengths f and transition moments X, Y

Compared	E_{calc}	E_{obs} [a]						f_{calc}	f_{obs} [a]						X	Y
		1	2	3	4	5	6		1	2	3	4	5	6		
Ia	2.72	2.83	2.89	2.86	2.87	2.97	2.98	0.36	0.67	0.68	0.69	0.70	0.68	0.74	−0.71	−0.50
	4.17	4.28	4.34	–	–	4.34	4.28	0.28	0.28	0.29	–	–	0.26	0.27	−0.61	−0.10
	4.56	4.63	4.74	–	4.47	4.74	4.93	0.36	0.28	0.29	–	0.28	0.27	0.28	−0.56	0.38
	6.03	5.91	–	–	–	–	–	0.06	0.39	–	–	–	–	–	−0.24	0.07
Ib	2.91	2.75	2.76	2.81	2.80	2.86	2.87	0.68	0.78	0.79	0.79	0.76	0.82	0.82	1.14	−0.15
	4.27	4.08	4.11	–	–	4.14	4.14	0.16	0.29	0.30	–	–	0.28	0.27	0.41	0.21
	4.76	4.63	4.74	4.67	4.43	4.74	4.81	0.34	0.30	0.30	0.32	0.47	0.30	0.31	0.48	0.42
	5.99	5.88	–	–	–	–	–	2.24	0.45	–	–	–	–	–	1.02	1.05
Ic	2.72	2.75	2.60	2.61	2.63	2.71	2.87	0.03	0.73	0.72	0.70	0.75	0.66	0.80	−0.23	−0.06
	4.20	4.08	–	–	–	–	4.14	0.77	0.29	–	–	–	–	0.27	0.51	0.89
	4.72	4.63	4.60	–	4.74	4.67	4.70	0.05	0.30	0.38	–	0.26	0.28	0.31	0.22	0.11
	5.76	5.91	–	–	–	–	–	0.15	0.39	–	–	–	–	–	0.25	−0.30
Id	2.74	2.75	2.74	2.74	2.86	2.91	2.87	0.02	0.80	0.87	0.88	0.77	0.75	0.82	−0.20	−0.07
	4.21	4.25	4.22	–	4.25	4.25	4.19	0.77	0.31	0.33	–	0.34	0.29	0.30	0.51	0.88
	4.74	4.53	4.60	–	–	4.81	4.70	0.06	0.30	0.32	–	–	0.28	0.30	0.24	0.12
	5.77	5.91	–	–	–	–	–	0.16	0.52	–	–	–	–	–	0.26	−0.31
Ie	2.72	2.70	2.71	2.75	2.82	2.90	2.86	0.04	0.23	0.19	0.21	0.22	0.29	0.24	0.28	0.08
	4.21	–	4.17	–	4.01	4.17	4.14	0.82	–	0.10	–	0.05	0.10	0.09	0.51	0.92
	4.78	–	4.60	–	–	4.81	5.05	0.05	–	0.11	–	–	0.11	0.12	−0.24	−0.05
	5.75	5.91	–	–	–	–	–	0.11	0.18	–	–	–	–	–	−0.21	0.26
If	2.67	2.68	2.71	2.63	2.78	2.82	2.82	0.09	0.39	0.39	0.36	0.45	0.42	0.38	0.43	−0.02
	4.14	–	4.17	–	4.01	4.06	4.08	0.60	–	0.06	–	0.08	0.14	0.24	−0.38	−0.83
	4.84	–	4.81	–	–	4.97	5.01	0.07	–	0.07	–	–	0.16	0.18	−0.01	−0.28
	6.06	5.91	–	–	–	–	–	0.13	0.28	–	–	–	–	–	−0.30	0.18
Ig	2.44	2.53	2.47	2.49	2.65	2.65	2.80	0.56	0.12	0.16	0.09	0.13	0.15	0.14	−0.71	0.90
	4.11	4.28	4.28	–	–	–	–	0.34	0.06	0.06	–	–	–	–	0.33	0.60
	4.45	–	4.67	4.53	–	4.40	4.37	0.09	–	0.06	0.07	–	0.07	0.07	0.17	−0.30
	5.48	5.86	–	–	–	–	5.31	0.12	0.24	–	–	–	–	0.13	−0.21	−0.29

[a] In solvents: 1, ethanol; 2, isopropanol; 3, acetone; 4, chloroform; 5, dioxane; 6, cyclohexane.

However, the absorption spectra in various solvents are influenced by solvation and/or dielectric constant of the solvents D, or more precisely a function $f(D)$ or $\phi(D)$, where

$$f(D)=\frac{2(D-1)}{2D+1}$$

$$\phi(D)=\frac{D-1}{D+2}$$

The plots of $(D-1)/(D+1)$, $f(D)$ and $\phi(D)$ against the wavelength (λ_{max} in nm) show a linear relationship if the dielectric constant is the only parameter governing the band shift in such solvents. In our study, these plots show a deviation from linearity indicating that the dielectric constant is not the only parameter governing the band shift. This may be attributed to a solute–solvent interaction which may overcome the dielectric effect of these solvents, in other words solvation has occurred.

The calculated π–π^* spectral transition energies E for cyanoformazans Ia–g are given in Table 2 along with the oscillator strength f. The experimental values E_{obs} and f_{obs} are also included in Table 2. Observed oscillator strengths f_{obs} were calculated from the experimental data applying the following relations [23]:

$$f_{obs}=4.32\times10^{-9}\times\epsilon_{max}\times1.06\ \mathrm{h}$$

$$f_{obs}=2.0\times10^{-5}\times\epsilon_{max}\ \text{(for shoulder)}$$

where ϵ_{max} is the molar absorptivity and h is the half band width in cm^{-1}. It is clear that the present data are in good agreement with the experimental ones. The best fit between calculated and observed values was achieved with ethanol, i.e. the quality of fit depends, to some extent, on the solvent polarity. According to Koopmans theorem [24], the ionization potential (IP) can be approximated by the highest occupied molecular orbital energy (HOMO). Ionization potentials were calculated using the relation

$$\mathrm{IP}=a+b(h\nu_{max})$$

where a and b are constants [25]. As may be seen in Table 3 the IP_{calc} and IP_{obs} are well fitted, while IPs are reasonably correlated with HOMO. The following relation between IP and HOMO is commonly stated in the literature:

$$\mathrm{IP}=-(\mathrm{HOMO}+C)$$

where C is a correction term. Birss and Das Gupta [26] used a value of C of 1.88 eV in their predictions of the ionization potential of a large number of aromatic hydrocarbons and heterocyclic systems. The values of HOMO are also correlated with the lowest observed transition energies $h\nu_{max}$ (HOMO → LUMO) in organic solvents. Calculated charge densities are shown in Table 4. It may be seen that similar charge density distribution on the

TABLE 3

Observed, calculated ionization potential energies (IP_{obs}, IP_{calc}) of highest occupied molecular orbital (HOMO), binding energy (BE) and $h\nu_{max}$ in various organic solvents [a]

Compound	IP_{obs} (eV)	IP_{calc} (eV)	HOMO	BE	$h\nu_{max}$ (HOMO → LUMO) (eV)					
					1	2	3	4	5	6
Ia	7.09	7.02	7.107	−949.121	2.83	2.89	2.86	2.87	2.97	2.98
Ib	7.12	7.15	7.692	−1088.217	2.75	2.76	2.81	2.80	2.86	2.87
Ic	7.01	7.02	6.742	−1278.558	2.75	2.60	2.61	2.63	2.71	2.87
Id	7.03	7.03	6.772	1274.304	2.75	2.74	2.74	2.86	2.91	2.87
Ie	7.01	7.02	6.729	−1267.492	2.70	2.71	2.75	2.82	2.90	2.86
If	6.99	6.98	6.25	−1260.067	2.86	2.71	2.63	2.78	2.82	2.82
Ig	6.84	6.82	6.065	−1603.318	2.53	2.47	2.49	2.65	2.65	2.80

[a] Solvents as in Table 1.

TABLE 4

Hammet constant σ and electron densities q of cyanoformazans Ia–g

Compound	X	σ	q			
			ϕ_1	ϕ_2	FR	X
Ia	H	0.00	6.0359	5.7803	8.1838	–
Ib	p-CH_3	−0.17	5.8114	5.9061	7.7327	0.9701
Ic	p-OCH_3	−0.27	6.1101	5.8305	8.1994	3.8600
Id	p-Cl	+0.23	6.1142	5.8263	8.1982	3.8711
Ie	p-Br	+0.39	6.1224	5.8312	8.1998	3.8594
If	p-I	+0.28	6.1199	5.8385	8.2008	3.8408
Ig	o-COOH	–	6.0403	5.7759	8.1100	8.0738

TABLE 5

Stretching frequencies $\bar{\nu}$, corresponding force constants F_{str} and their bond orders BO

Band	Ia			Ib			Ic		
	$\bar{\nu}$	F_{str}	BO	$\bar{\nu}$	F_{str}	BO	$\bar{\nu}$	F_{str}	BO
C≡N (stretch)	2230	18.92	0.797	2210	18.58	0.896	2215	18.70	0.791
C=N (stretch)	1540	9.02	0.547	1530	8.91	0.647	1530	8.91	0.545
N=N (stretch)	1440	8.55	0.849	1440	8.55	0.829	1400	8.08	0.848
C–N (asym)	1275	6.19	0.413	1280	6.23	0.458	1270	6.14	0.41
C–N (sym)	1190	5.39	0.413	1140	4.95	0.458	1190	5.39	0.41

[a] $\bar{\nu}$, F_{str} and BO of C=O for derivative Ig are 1730, 12.09 and 0.639, respectively.

phenyl rings (ϕ) was observed, while the charge density on nitrogen atoms of formazan skeleton (FR) is higher. Hence electrophilic attack is most probable on these centres [27]. The difference in electron densities on the phenyl ring ϕ and on the formazan skeleton is correlated with the electron withdrawing or donating power of the substituent scaled on the basis of the Hammet substituent σ.

Infrared spectra

The IR spectra of the diphenyl cyanoformazans (Fig. 2) are characterized by the band due to the stretching of the NH group, which appears in the wavenumber range 3300–3100 cm^{-1} indicating its participation in hydrogen bonding. A medium or weak absorption band is observed in all the formazans at about 1450–1440 cm^{-1}, so that at first glance the present results harmonize with those of Le Fevre et al. [28] for azobenzene and various other azo compounds. However, their connection with –N=N– group can be discounted. The C≡N group in the cyanoformazans gives rise to a sharp absorption near 2260–2200 cm^{-1} [29]. The following is an attempt to correlate these IR stretching frequencies in terms of their force constants F_{str} (in mdyne Å^{-1}) with the corresponding calculated bond orders (Table 5). It can be seen that the bond order of C≡N (0.79–0.89), C=N (0.55–0.66) and C–N (0.41–0.45) parallel to the force constants of their stretching frequencies bands which appear at 2210–2230 cm^{-1}, 1530–1540 cm^{-1} and 1270–1280 cm^{-1}, respectively.

Thermal conductivity

Figure 3 shows the temperature dependence of conductivities of symmetric substituted derivatives with electron withdrawing functional groups Cl, Br, I and COOH (1d–g), in which all samples show typical semiconducting behaviour. At low temperatures all derivatives show significant deviation from linear dependence. This is most likely to be due to the existence of two

Id			Ie			If			Ig [a]		
$\bar{\nu}$	F_{str}	BO	$\bar{\nu}$	F_{str}	BO	$\bar{\nu}$	F_{str}	BO	$\bar{\nu}$	F_{str}	BO
2220	18.75	0.791	2210	18.58	0.791	2215	18.70	0.790	2215	18.70	0.848
1540	9.02	0.545	1530	8.91	0.544	1530	8.91	0.544	1540	8.91	0.549
1430	8.43	0.848	1420	8.31	0.848	1420	8.31	0.848	1450	8.67	0.822
1270	6.14	0.41	1270	6.14	0.41	1270	6.14	0.410	1270	6.14	0.453
1190	5.39	0.41	1190	5.39	0.41	1190	5.39	0.410	1190	5.39	0.453

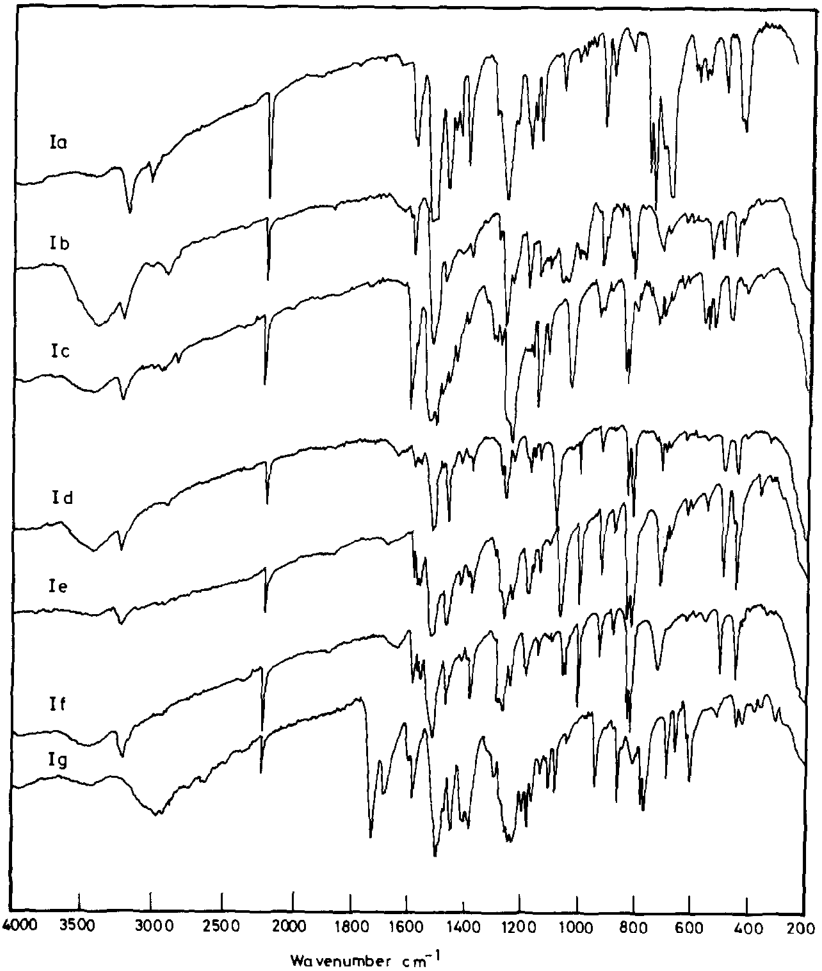


Fig. 2. Infrared absorption spectra of 1,5-bis-diphenyl-3-cyanoformazan and its derivatives Ia–g.

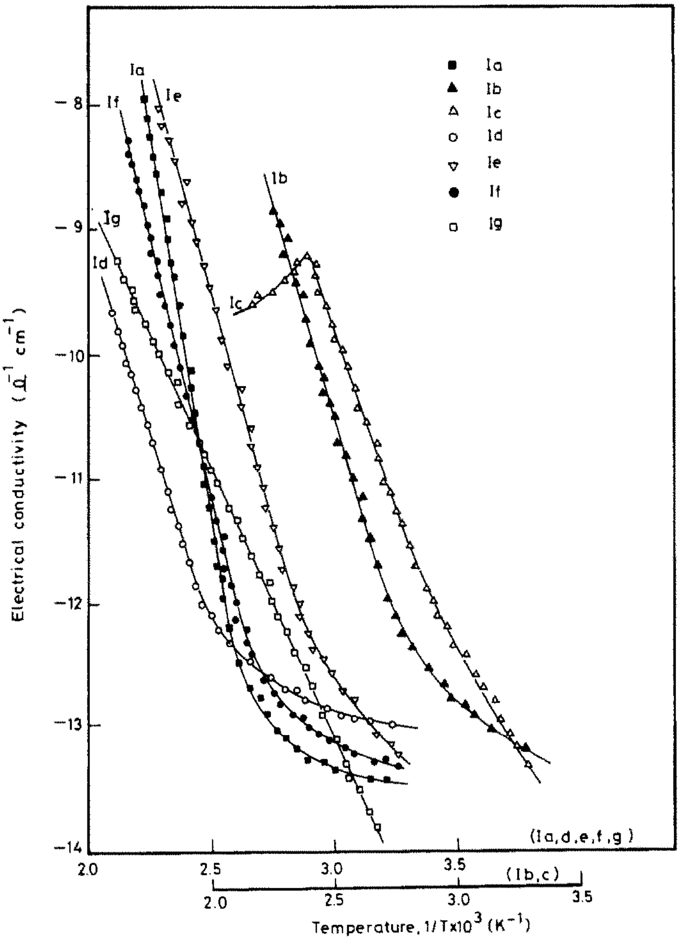


Fig. 3. Variation of electrical conductivity as a function of reciprocal absolute temperature for solid formazans Ia–g.

different conduction mechanisms. At low temperatures, we are dealing with a pure extrinsic conduction, where the conduction is mainly due to the empty states (positive holes) formed by transition of electrons to the acceptor levels. This process is strongly connected to the enhancement of the delocalization of π-electrons, usually characterized by a low activation energy. At higher temperatures, where the intrinsic region is reached, the activation energy should be higher (Table 6). Such a situation is connected with the transition of π-electrons from the valence band to the lowest empty π-states in the conduction band; in other words, it is assumed that the electrons tunnel to an equivalent empty level of a neighbouring molecule, where the positive holes moves from one molecule to another in the cathodic direction. The substituents may facilitate the conduction process, which would be in agreement with the experimented data, in which it is observed

TABLE 6

Activation energy ΔE (eV) over the interinsic temperature range and calculated dipole moments [a] (XMU, YMU) of cyanoformazan derivatives Ia–g

Compound	ΔE	Dipole moment	XMU	YMU
Ia	2.54	21.2864	20.7718	−4.6521
Ib	1.38	32.5262	31.2970	−8.8575
Ic	1.19	19.8396	19.0590	−5.5983
Id	1.29	19.9366	19.1774	−5.4497
Ie	1.48	19.8826	19.1116	−5.4832
If	1.70	19.7725	18.9778	−5.5491
Ig	0.87	25.9862	23.4004	−11.3006

[a] Calculated using PPP CI.

that the activation energy decreases with increasing electronegativity of the substituent, i.e. Cl > Br > I. The introduction of a COOH group in the *ortho* position of the phenyl rings led to the decrease of activation energy in the intrinsic region. This can be attributed to the increase in the delocalization of π-electrons system over the whole molecule with the carboxylic group in this position. In the case of electron-donating substituents (Ib–c) the mechanism of the electron delocalization is different, involving intramolecular charge migration from the phenyl ring to the cyanoformazan skeleton. This means that an electron-donating substituent will enhance the flow of charge in this direction, which in turn will lead to a lowering of the activation energy with respect to the unsubstituted formazan. This is supported by the charge density distribution (Table 4).

Correlations were found between the activation energy ΔE and the theoretically calculated dipole moments. The derivative Ig has the lowest activation energy and highest dipole moments. For the halogenated derivatives (Id–f) the activation energy decreases as the dipole moment is increased. For the derivatives Ib–c the change in the dipole moment is inversely related to that of the activation energy. This may be due to mutual inhibition between the processes of charge migration and the reorientation of dipole moments within the intrinsic temperature range, which has the effect of increasing the activation energy.

Thus, as expected, the variation of activation energy is inversely related to the binding energy for the derivatives Ia–g (Table 3).

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