

STUDIES OF INTER- AND INTRA-MOLECULAR DONOR-ACCEPTOR INTERACTIONS—IV INTRAMOLECULAR CHARGE TRANSFER PHENOMENA IN SUBSTITUTED N-ARALKYL-PYRIDINIUM IONS*

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Abstract—The absorption spectra of compounds with the general structure $D-(CH_2)_n-A$, in which D is a substituted Ph group and A a 4-cyanopyridinium group show long-wavelength absorption not attributable to transitions within the separate chromophores. This absorption at long-wavelength results from an intramolecular Charge Transfer (CT) interaction between D and A. The CT nature of the absorption is proved by the linear relationship between the ionization potential of D and the energy of the CT transition. Furthermore the intramolecular CT is comparable with the intermolecular CT interaction between analogous D and A systems, both in transition energy and solvent dependence.

The appearance of an intramolecular CT band in the spectra of compounds with $n = 1$ can qualitatively be predicted from the character of the highest and one but highest filled molecular orbital in the D part of the molecule. Simple MO calculations indicate that the 4-cyanopyridinium ion has stronger acceptor properties than the 2- and 3-cyano isomers, which agrees with our previous findings,³ for intermolecular CT complexes.

INTRODUCTION

THE CONCEPT of intramolecular CT has successfully been used in the description of the interaction between directly conjugated chromophores.^{5,6} We have investigated¹⁻⁴ the possibility of intramolecular CT interaction between an electron donor (D) and an electron acceptor (A), connected by a (saturated) carbon chain in molecules of the type $D-(CH_2)_n-A$ where direct mesomeric interaction through this chain is excluded.

In these non-conjugated systems the interaction between D and A will be weak, leaving the basic electronic structure of D and A unaltered. This situation is comparable with the well known⁷ intermolecular CT interaction between separate D and A molecules.

Linking of D and A by a chain may strongly influence their relative orientation and therefore such systems may give some insight in the conformation of intermolecular CT complexes in solution, which is in many cases still an unsolved problem.^{8,9}

Several studies of molecules containing non-conjugated D and A moieties have been reported in the literature. Russian workers have synthesized a variety of compounds containing non-conjugated homocyclic aromatic D and A groups.¹⁰ White¹¹ studied the absorption spectra of $p-O_2NC_6H_4-(CH_2)_n-C_6H_4-p-NH_2$ ($n = 1, 2, 3$)

* For previous papers in this series see Refs. 1-4.

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and concluded that intramolecular CT interaction occurred. Recently Ōki and Mutai¹² reported intramolecular CT phenomena in the isomeric compounds $p\text{-O}_2\text{NC}_6\text{H}_4\text{-(CH}_2\text{)}_n\text{-NHC}_6\text{H}_5$.

In all these studies the intramolecular CT absorption band is either obscured or distorted by the absorption of the separate D and A moieties. The intensity and the position of the CT band can only be obtained by subtraction^{11, 12} and as we show in this paper this may lead to erroneous results. A more suitable system containing naphthoquinone as an acceptor¹³ has recently been reported to show intramolecular CT bands with a discrete maximum.

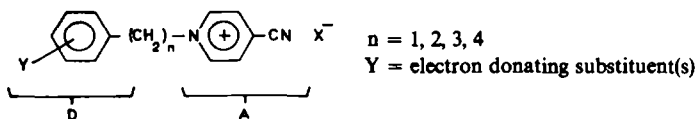
CT interaction is not only possible between neutral D and A species, but also between ions or between neutral species and ions.¹⁴ Especially the acceptor properties of the biochemically important nicotinamidium ion have been reported.¹⁵ Evidence for intramolecular CT, involving a pyridinium ion as the acceptor, was first found by Kosower¹⁶ *et al.* in the spectrum of N-[(*p*-anisyl) methyl]-4-carbomethoxy-pyridinium perchlorate.

A series of systems containing the nicotinamidium ion as an acceptor was studied by Shifrin,¹⁷ who used the difference method for evaluation of the position and intensity of the CT bands.

In a previous paper³ we have reported the acceptor properties of some substituted pyridinium ions. From the intermolecular CT interaction of these ions with some neutral organic donors we concluded that especially the N-alkyl-4-cyanopyridinium ion possesses strong acceptor properties. In another paper¹ we reported the absorption spectra of some compounds containing the 4- or 3-cyanopyridinium ion as an acceptor and a substituted Ph group as a donor, connected by a chain of one to four methylene groups. Two of these compounds—both containing the 4-cyanopyridinium group—showed an intramolecular CT band with a discrete maximum distinctly separated from the original absorption bands of the isolated D and A groups.

RESULTS AND DISCUSSION

The excellent acceptor properties of the 4-cyanopyridinium ion led us to synthesize² a larger number of compounds with this acceptor and various donor groups.



All compounds do at least show a shoulder or a long-wavelength absorption tail above 300 nm, and many of the compounds with $n = 1$ or 2 show "free" absorption maxima in this region undisturbed by the separate D and A groups which absorb at shorter wavelength.

In Tables 1 and 2 the absorption maxima in the region above 300 nm for the compounds with $n = 1$ and 2 are compiled.

Intramolecular character of the absorption bands

A major difficulty in the study of intramolecular CT interaction in compounds with the general structure $\text{D-(CH}_2\text{)}_n\text{-A}$ is the possibility of additional intermolecular CT interaction, which can be avoided by the use of sufficiently dilute solutions.

TABLE I. POSITION, INTENSITY AND BANDWIDTH OF INTRAMOLECULAR CT BANDS FOR COMPOUNDS WITH D AND A LINKED BY ONE METHYLENE GROUP

Parent donor molecule	No* of Compound	Water (25°)				Ethanol (96%) (25°)							
		Y	X	λ_{\max} (nm)	$\tilde{\nu}_{\max}$ (kK)	$h\nu$ (eV)	$\Delta\tilde{\nu}_{\dagger}$ (kK)	$\epsilon_{\max}\ddagger$	λ_{\max} (nm)	$\tilde{\nu}_{\max}$ (kK)	$h\nu$ (eV)	$\Delta\tilde{\nu}_{\dagger}$ (kK)	$\epsilon_{\max}\ddagger$
Benzene	XLVII	H	Cl	—	—	—	—	—	—	—	—	—	—
Toluene	LI	4-Me	Cl	—	—	—	—	—	—	—	—	—	—
Anisole	LII	4-MeO	Cl	327	30.58	3.79	3.33	475	337.5	29.63	3.67	3.00	535
	LIII	3-MeO	Cl	—	—	—	—	—	—	—	—	—	—
	LIV	2-MeO	Cl	325	30.77	3.81	3.74	385	331	30.21	3.74	3.22	429
1,2-Dimethoxybenzene	LV	2,3-diMeO	Cl	—	—	—	—	—	—	—	—	—	—
	LVI	3,4-diMeO	Cl	348	28.73	3.56	3.54	309	364	27.47	3.40	3.32	325
1,3-Dimethoxybenzene	LVII	2,6-diMeO	Cl	321.5	31.10	3.85	3.32	660	323	30.96	3.84	3.18	699
	LVIII	3,5-diMeO	Cl	—	—	—	—	—	—	—	—	—	—
	LIX	2,4-diMeO	Cl, OTos	351.5	28.45	3.53	3.32	(500)	361.5	27.66	3.43	2.97	(500)
1,4-Dimethoxybenzene	LX	2,5-diMeO	Cl	369.5	27.06	3.35	3.53	299	384	26.04	3.23	3.10	322
1,2,3-Trimethoxybenzene	LXI	3,4,5-triMeO	Cl	324	30.86	3.82	3.80	470	333	30.03	3.72	3.95	457
1,2,4-Trimethoxybenzene	LXII	2,4,5-triMeO	Cl	389	25.71	3.19	3.56	420	406	24.62	3.05	3.31	440
1,3,5-Trimethoxybenzene	LXIII	2,4,6-triMeO	Cl, OTos	356	28.09	3.48	3.34	(750)	366	27.32	3.39	2.99	(750)
Mesitylene	LXIV	2,4,6-triMe	Cl	—	—	—	—	—	—	—	—	—	—

* Numbers correlate with those from our previous reports.²† $\Delta\tilde{\nu}_{\dagger}$ gives the distance in wavenumber between the band maximum and the long-wavelength half height position.‡ Values in parentheses less reliable because of instability.²

TABLE 2. POSITION, INTENSITY AND BANDWIDTH OF INTRAMOLECULAR CT BANDS FOR COMPOUNDS WITH D AND A LINKED BY AN ETHYLENE GROUP

Parent donor molecule	No* of Compound		Water (25°)					Ethanol (96%) (25°)						
			λ_{\max} (nm)	$\bar{\nu}_{\max}$ (kK)	$h\nu$ (eV)	$\Delta\bar{\nu}_4^\dagger$ (kK)	ϵ_{\max}	λ_{\max} (nm)	$\bar{\nu}_{\max}$ (kK)	$h\nu$ (eV)	$\Delta\bar{\nu}_4$ (kK)	ϵ_{\max}		
Benzene	LXVII	H	—	—	—	—	—	—	—	—	—	—	—	—
Anisole	LXVIII	4-MeO	327	30.58	3.79	3.84	755	338	29.59	3.67	3.41	801		
1,2-Dimethoxybenzene	LXIX	3,4-diMeO	—	—	—	—	—	357	28.01	3.47	3.86	620		
1,3-Dimethoxybenzene	LXX	2,4-diMeO	354.5	28.21	3.50	3.82	660	364	27.47	3.40	3.49	749		
	LXXII	3,5-diMeO	—	—	—	—	—	—	—	—	—	—		
1,4-Dimethoxybenzene	LXXI	2,5-diMeO	370	27.03	3.35	3.99	285	380	26.32	3.26	3.67	305		
1,2,4-Trimethoxybenzene	LXXIII	2,4,5-triMeO	395.5	25.28	3.13	3.78	417	407	24.57	3.04	3.63	447		
1,3,5-Trimethoxybenzene	LXXIV	2,4,6-tr:MeO	374	26.74	3.31	3.27	790	387	25.84	3.20	3.01	840		
Mesitylene	LXXV	2,4,6-triMe	322.5	31.01	3.84	3.61	1120	326	30.67	3.80	3.27	1280		

* Numbers correlate with those from our previous reports.²

† $\Delta\bar{\nu}_4$ gives the distance in wavenumber between the band maximum and the half height position at the long-wavelength side.

In our study³ of intermolecular CT interaction between the N-alkyl-4-cyanopyridinium ion and OMe substituted benzene derivatives, we evaluated the equilibrium constants and molar extinction coefficients for some of these complexes. The equilibrium constants (K) in ethanol are in the order of 0.3 l. mole⁻¹ and the molar extinction coefficients (ϵ) range from 337 to 976.

For an x-molar solution of D and A with $K = 0.3$ l. mole⁻¹ and ϵ as high as 1000, the absorbance (E) of the complex (DA) amounts to approximately $300 x^2$ in a cell of 1 cm pathlength. Thus for systems with the structure D-(CH₂)_n-A we expect that at concentrations below 10⁻² M the contribution of intermolecular CT to the measured absorbance is negligible ($E < 0.03$). Indeed it was found that all compounds from Tables 1 and 2 obey Beers Law at concentrations below 10⁻² M (range studied 10⁻²–10⁻⁴ M). Most spectra were measured at 10⁻³ M, in 1 cm cells.

There is another factor which may contribute to the absence of intermolecular interaction in the systems studied here.

If two molecules of the structure D-(CH₂)_n-A approach one another so as to give intermolecular CT interaction, then at the same time the positively charged A parts of both molecules do approach each other, which will be unfavourable because of Coulomb repulsion. This Coulomb repulsion does not exist for the normal intermolecular interaction between the separate (neutral) DH and (positively charged) ACH₃ moieties.

Influence of the anion

It is well known that some anions give a strong CT interaction with pyridinium ions. This interaction, which is particularly strong in apolar solvents, has been studied for the sulfoxylate¹⁸ the cyanide¹⁹ and especially for the iodide²⁰ ion. The interaction with less polarizable anions, in polar solvents seems to be negligible.

In order to prevent disturbance of our measurements by the influence of the anion, we have used the chloride or the *p*-toluenesulphonate ion. These anions do not absorb in the region above 300 nm, nor do they give any detectable interaction with the 4-cyanopyridinium ion in dilute aqueous or ethanolic solutions.

To ensure that the anion has no influence on the observed intramolecular CT bands either, we have measured the spectrum of the N-[2-(*p*-anisyl)-1-ethyl]-4-cyanopyridinium ion in water at a concentration of 10⁻³ M with three different non-polarizable counter ions, i.e. the chloride, the nitrate and the sulphate ion (cf. Experimental).

In the region of the intramolecular CT band (between 320 and 400 nm) no specific influence from the anion on the absorption spectrum could be observed.

Furthermore in all (five) instances investigated the spectra of pyridinium *p*-toluenesulphonates and the corresponding pyridinium chlorides (readily obtainable from the first by anion exchange²) were found to be identical at least in water or ethanol in the region above 300 nm.

Solvent effects

The CT character of the long-wave absorption bands of compounds D(CH₂)_nA is supported by their broad and structureless shape and by the influence of solvent polarity.

In Fig. 1 we have plotted the wavenumber (in kK) of the long-wave absorption

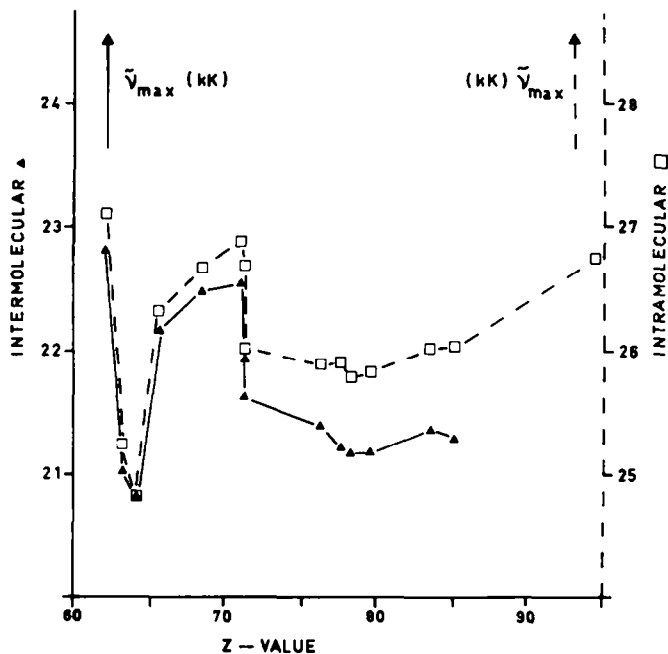


FIG. 1 Plot of solvent polarity (Z -value) versus position of *intermolecular* CT band (for the system *N,N*-dimethylaniline/*N*-(*n*-decyl)-4-cyanopyridinium *p*-toluene sulphonate) and versus position of *intramolecular* CT band for LXXIV.

Cf. Ref. 3 for the Z -value of the solvents employed.

band of *N*-[2-(2,4,6-trimethoxyphenyl)-1-ethyl]-4-cyanopyridinium *p*-toluenesulphonate (LXXIV), against the Z value³ of the solvent. Apparently there is no simple relationship between these parameters, for reasons mentioned before.³

The same is true (cf. Fig. 1) when we make a similar plot for the *intermolecular* CT band of *N,N*-dimethylaniline and *N*-(*n*-decyl)-4-cyanopyridinium *p*-toluenesulphonate in the same solvents. However, we see that the two plots are strikingly analogous and this strongly supports the CT character of the long-wave absorption band in LXXIV (cf. also our earlier work in Ref. 3).

Correlation between CT and ionization potentials

For the *intermolecular* interaction of the *N*-methyl-4-cyanopyridinium ion as an acceptor with polymethoxy-substituted benzenes as donors in 96% ethanol we have shown³ that a linear relationship exists between the ionization potential of the donor (I_D)* and the energy ($h\nu$) of the corresponding *intermolecular* CT transition.

$$h\nu = 0.87 I_D - 3.47 \quad (\text{eV}) \quad (1)$$

This linear relationship supports the CT character of the observed transitions.

To compare *inter*- and *intramolecular* CT, we will assume that in compounds with the structure $D-(CH_2)_n-A$ the donor properties of the *D* part and the acceptor properties of the *A* part are practically equal to those of the isolated DH and ACH_3 species.

* The ionization potential of most donors was measured by an indirect method cf. Appendix 1.

This assumption is reasonable since we have shown³ that even for compounds with $n = 1$ the interaction between D and A through the methylene chain is very weak. Thus we have plotted the energy (in eV) of the intramolecular CT transitions versus the ionization potential (cf. Appendix 1) of the parent donor molecules, both in water as a solvent (Fig. 2) and in 96% ethanol (Fig. 3). From the values plotted in Fig. 2 and Fig. 3 the following relations were evaluated by the method of least squares:

$$\text{In water:} \quad h\nu = 0.83 I_D - 3.00 \quad (2)$$

$$\text{In ethanol (96\%):} \quad h\nu = 0.85 I_D - 3.27 \quad (3)$$

For comparison the line corresponding with Eq. (1) has also been drawn in Fig. 3 and it will be noted that the correlation between inter- and intramolecular CT holds reasonably well.* Again these data support the earlier conclusion that intramolecular CT is involved.

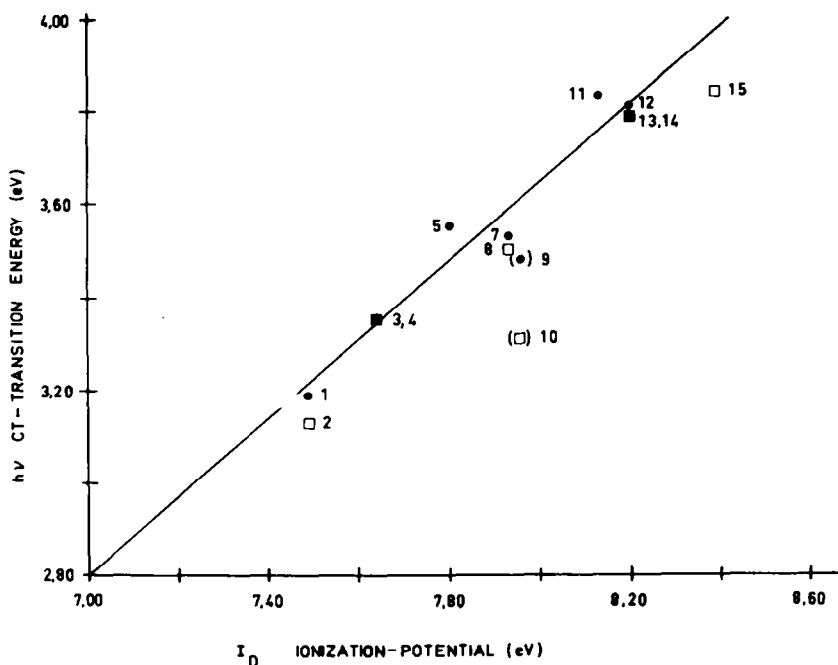


FIG. 2 Linear relationship (cf. formula-2) between donor ionization potential (I_D) and the energy ($h\nu$) of the intramolecular CT transitions for the compounds from Table 1 (●) and Table 2 (□), in water as a solvent.

(1) LXXII, (2) LXXIII, (3) LX, (4) LXXI, (5) LVI, (6) LXIX, (7) LIX, (8) LXX, (9) LXIII, (10) LXXIV, (11) LXI, (12) LIV, (13) LII, (14) LXVIII, (15) LXXV. Values in parentheses were discarded in the calculation of formula-2.

* From the ionization potential of benzene (9.245 eV) and Eq. (2) a wavelength of 266 nm is calculated for the intramolecular CT band in compounds of the structure $C_6H_5-(CH_2)_n-A$. This value differs markedly from the estimated¹ for such compounds with a "difference spectrum" method (298 nm), showing the unreliability of this method. The unusual relation found by Shifrin¹⁷ between $h\nu$ and I_D probably resulted from the use of this difference method.

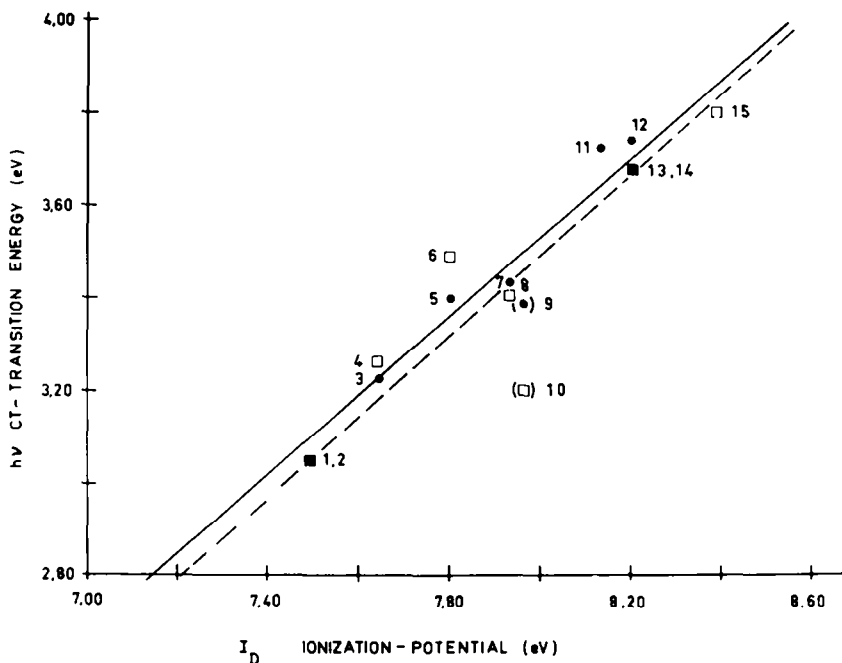


FIG. 3 Solvent: ethanol (96%). For other details cf. comment with Fig. 2.

The drawn line corresponds with formula-3; the dotted line refers to intermolecular CT (formula-1).

Intramolecular CT and structural effects

The correlation between inter- and intramolecular CT, as shown in the previous sections, suggests that the intramolecular CT has the same "through-space" character as the intermolecular interaction. This is substantiated by the observation that the position of the intramolecular CT band does not (with only one exception) depend strongly on the length of the (poly)methylene chain. This indicates that the interaction between D and A does not involve the σ -electrons of the (poly)methylene chain, which is also obvious from the observation that the intensity of the intramolecular CT band sometimes increases when the chain is lengthened from one to two methylene groups.

Of course the nature of the methylene chain influences the orientation of D towards A. Since the broad shape of CT bands is associated with the relatively loose configuration of CT complexes in general,²¹ it is not unexpected that the intramolecular CT bands of the compounds with one methylene group (cf. Table 1) are somewhat sharper than the more flexible homologues with two methylene groups (cf. Table 2).

For the intermolecular complexes between the N-alkyl-4-cyano-pyridinium ion and methoxybenzenes we have assumed the usual configuration between aromatic donors and acceptors, i.e. a structure with the planes of both molecules approximately parallel.³

It seems reasonable to suppose that the positively charged N atom of the pyridinium system will approach the most electron rich position of the donor. Such an approach of the most electronegative site of the acceptor and the most electron rich site of the donor has been proposed before and was found in several instances.^{22, 23}

The complexes between methoxybenzenes and the N-alkyl-4-cyano-pyridinium ion are rather weak³ ($\Delta H \approx -1.5$ kcal. mole⁻¹). In compounds with the structure D-(CH₂)_n-A, the tendency towards complex formation between D and A will generally be too small to overcome torsional or rotational barriers imposed by the methylene chain.

One methylene group between donor and acceptor. Especially in the compounds DCH₂A (cf. Table 1) the relative orientation of D and A is fairly rigid and differs strongly from the configuration proposed for the intermolecular complexes. The conformation depicted in Fig. 4 allows only some overlap between the π -electron systems of D and A in a small region. Nevertheless the intensity of the CT bands for the compounds from Table 1 is in the same order of magnitude as the intensity of the CT bands for intermolecular complexes between the N-methyl-4-cyanopyridinium ion and methoxybenzenes.³

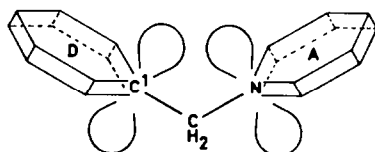


FIG. 4 Conformation of compounds D-CH₂-A, in which overlap between the C₁ *p*-orbital of D and the ring-N *p*-orbital of A is possible.

In the MO picture, a CT transition involves the excitation of an electron from the highest occupied molecular orbital (HOMO) of D (ψ_D) to the lowest vacant orbital of A (ψ_A). From Fig. 4 it can be inferred that overlap between the π -electron systems of D and A is practically limited to an overlap between the C₁ *p*-orbital of D and the nitrogen *p*-orbital of A. So the degree of overlap between ψ_D and ψ_A will be governed by the question whether or not in a LCAOMO description the atomic *p*-orbitals mentioned above contribute appreciably to ψ_D and ψ_A and this depends on the absolute values of their orbital coefficients as obtained from LCAOMO calculations. Our calculations, performed by the simple HMO method (cf. Appendix 2), indicate that the ring-N *p*-orbital contributes relatively strongly to the lowest vacant MO (ψ_A) of the 4-cyanopyridinium ion (cf. Table 5).

For the OMe substituted benzenes, the results of our calculations for the HOMO and the HOMO-1 are compiled in Table 4.

Our calculations show that it is possible to predict the occurrence of an intramolecular CT transition in the spectra of compounds D-CH₂-A from the orbital coefficient of the C atom by which the donor is attached to the -CH₂-A group, with fixed A and variable D.

For instance in anisole the orbital coefficients of the HOMO decrease in the order C₄ > C₂ > C₃ (cf. Table 4).*

Accordingly the intensity of the intramolecular CT band in the isomeric compounds LII (*para*), LIV (*ortho*) and LIII (*meta*) decreases in the same order. For the last compound no discrete CT maximum is observed, but there is only a weak absorption tail

* Note the (unavoidable) difference between the atom numbers in Table 4 and the headings of Tables 1 and 2.

TABLE 3. IONIZATION POTENTIALS (I_D) OF VARIOUS SUBSTITUTED BENZENES ESTIMATED FROM THE POSITION ($\bar{\nu}_{\max}$) OF THE FIRST CT BAND IN COMPLEXES WITH TETRACYANOETHYLENE IN DICHLOROMETHANE THROUGH THE RELATION²⁴

$$h\nu = 0.925 I_D - 5.12 \text{ (eV)}$$

For comparison the values obtained by photoionization measurements are included whenever available.

Substituents in benzene ring	$\bar{\nu}_{\max}$ (kK)	I_D (eV) from from CT	I_D (eV) photoionization ref. 37	I_D (eV) photoionization ref. 38, 39
—	25.8 ± 0.05	8.99	9.24 ± 0.02	9.245 ± 0.01
Me	24.5*	8.82	8.81	8.82
1,4-diMe	21.5*	8.42	8.44	8.445
1,3,5-triMe	21.4	8.39	8.41	8.39
MeO	19.7	8.18		8.20
1,2-diMeO	16.9	7.80		
1,3-diMeO	17.9	7.93		
1,4-diMeO	15.7	7.64		
1,2,3-triMeO	19.4	8.13†		
1,2,4-triMeO	14.6	7.49		
1,3,5-triMeO	18.1	7.96		
1,2,4,5-tetraMeO	12.8*	7.25		

* Our measurements, the other values for $\bar{\nu}_{\max}$ from Ref. 24.

† Unexpectedly high value explained from steric factors.^{24, 33}

above 300 nm (cf. Fig. 5). It is interesting to note, that the position of the CT band is roughly the same in all three isomers being governed mainly by the electron affinity of A and the ionization potential of D (cf. theoretical part). For the highly symmetric (D_{2h}) 1,4-dimethoxybenzene (hydroquinone dimethyl ether), which is the donor system in compound LX, the HOMO has the same absolute orbital coefficients on the four equivalent C atoms.

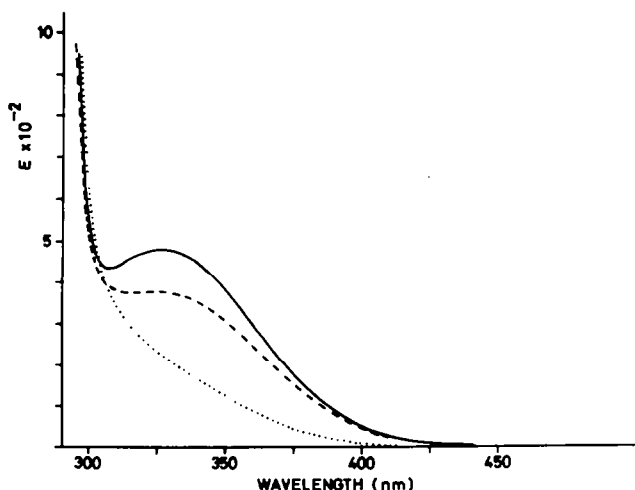


FIG. 5 Absorption spectra in water of the isomeric *N*-(methoxybenzyl)-4-cyanopyridinium chlorides: LII (—), LIII (.....), LIV (-----).

TABLE 4.

	C _{2v}	D _{2h}	C _{2v}	C _{2v}	C _s	D _{3h}	(C _{2v})
Energy (β)	+0.82741	+0.69236	+0.77270	+0.72609	+0.63737	+0.77270	+0.77270
Symmetry	$B_1 - S_z$	$B_{2g} - A_g S_z$	$A_2 - A_z$	$B_1 - S_z$	A''	$(B_1) - S_z$	
HOMO							
Orbital coefficient at various positions	1 +0.50825 2 +0.34897 3 -0.21951 4 -0.53059 5 -0.34675 6 -0.34675 7 -0.30049 8 -0.34675 9 -0.30049	+0.49117 +0.29023	+0.40163 -0.00000 -0.51977 +0.00000 -0.26179	+0.48311 +0.11038 -0.40296 -0.30339	+0.51171 +0.37871 -0.09246 -0.43764 -0.39203 +0.18778 -0.30042 -0.22234 +0.25694	+0.46376 +0.30009 -0.23188 -0.60018	
Energy (β)	+1.00000	+1.00000	+0.89734	+0.91923	+0.88581	+0.77270	
Symmetry	$A_2 - A_z$	$B_{1g} - S_g A_z$	$B_1 - S_z$	$A_2 - A_z$	A''	$(A_2) - A_z$	
HOMO-1							
Orbital coefficient at various positions	1 +0.00000 2 +0.50000 3 +0.50000 4 -0.00000 5 -0.00000 6 +0.00000 7 +0.00000 8 +0.00000 9 +0.00000	+0.00000 +0.50000	+0.28927 +0.64473 -0.21726 -0.48423 -0.20987	-0.22861 +0.57412 +0.29914 +0.16922	+0.08952 -0.36025 -0.61557 +0.18503 +0.34539 +0.49098 -0.06428 +0.25866 +0.13285	+0.00000 -0.51977 -0.40163 +0.00000	

Of more interest is the 1,3-dimethoxybenzene (resorcinol-dimethyl ether) donor, because it has a rather small difference in energy between the two highest occupied MO's (0.12464β). Accordingly for the intermolecular CT complex of this donor with tetracyanoethylene two strongly overlapping CT bands²⁴ can be observed. These two bands are attributed to CT transitions involving the HOMO and the HOMO-1 of the donor respectively. From Table 4 it can be seen that these two highest occupied MO's have quite different orbital coefficients at the three various ring positions. The HOMO in 1,3-dimethoxybenzene has a nodal plane through C₂ and C₅, while the HOMO-1 has its maximum coefficient at C₂. This gives the possibility to observe both possible intramolecular CT transitions *separately* in the various substitution isomers. In the C₄-substituted compound LIX the first CT band (resulting from a transition involving the HOMO) will be favoured, while in the C₂-substituted compound LVII the second CT band (involving the HOMO-1) will be. This is substantiated by the observation of a *discrete* CT band in the spectra of both compounds (cf. Fig. 6), which

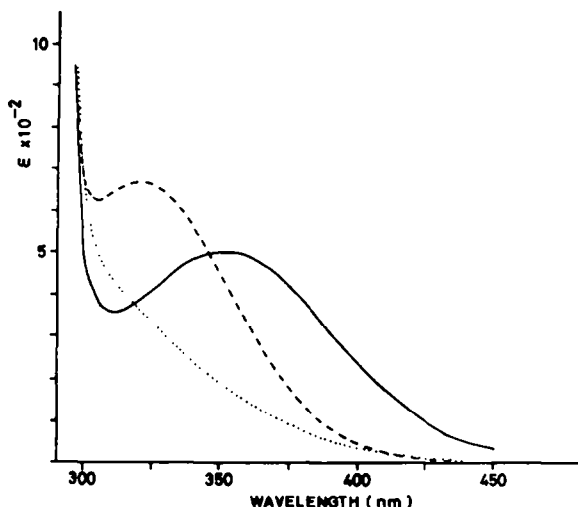


Fig. 6 Absorption spectra in water of: LVII (----), LVIII (....), and LIX (—).

is obviously not overlapped by another. In contrast with the anisole derivatives there is a large energy difference between the intramolecular CT transitions of the isomers LIX and LVII. This difference (0.41 eV) can be attributed to the energy difference between the HOMO and the HOMO-1 of the donor part, and is of the same order of magnitude as the energy difference between the two simultaneously observed intermolecular CT bands for the complex of 1,3-dimethoxybenzene with tetracyanoethylene ($0.595 \pm 0.14 \text{ eV}$).²⁴

For compound LVIII, which involves substitution at C₅, only an absorption tail with no discrete maximum is observed (cf. Fig. 6) since the coefficient of both the HOMO and the HOMO-1 is too small at C₅.

For the donor 1,2-dimethoxybenzene (veratrol) the energy difference between the two highest occupied MO's is larger than for 1,3-dimethoxybenzene (cf. Table 4). With tetracyanoethylene as an acceptor two slightly overlapping intermolecular CT bands have been observed with a separation of $0.79 \pm 0.04 \text{ eV}$.²⁴

From Table 4 it can be seen that at C_4 and C_5 both highest occupied MO's have approximately the same orbital coefficient. So we expect for compound LVI two CT bands to appear simultaneously. This is supported by the shape of the CT band for compound LVI (cf. Fig. 7). Although the band maximum is found at a relatively long-wavelength, the descent at its short wavelength side is remarkable small and the absorption at the short wavelength side rises steeper than can be explained from the absorption of the separate D and A moieties. This shows that there is another band at the short wavelength side of the first band, which we believe to be the second CT band.

For the parent compound with two methylene groups between D and A LXIX (cf. Table 2) the intensity ratio between the two CT bands is such that no discrete CT maximum can be observed in water as a solvent (cf. Fig. 7). For compound LV, which involves substitution at C_3 (or C_6), one would expect the intensity of the second CT band to increase, while the first band would be weak. In fact no long-wavelength CT band is observed for LV, but this does not prove anything because steric factors may play an important role, since a OMe group is flanked by two *ortho* substituents. As a result this OMe group will be rotated out of the plane of the Ph group, which strongly diminishes its electron donating properties.³³

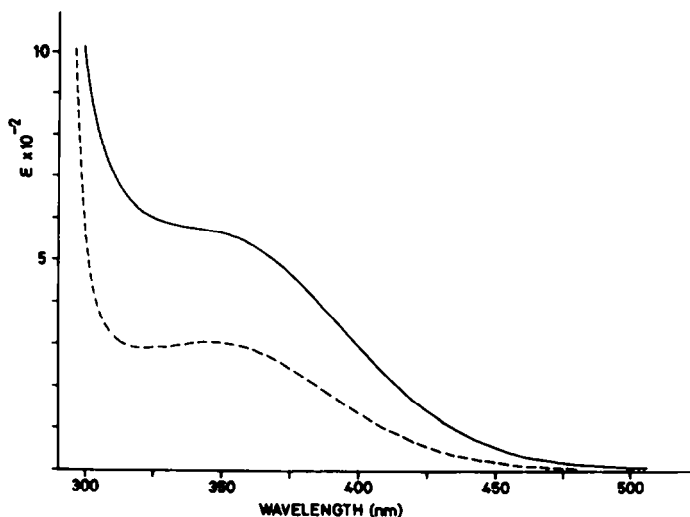


FIG. 7 Absorption spectra in water of: LVI (-----), and LXIX (—).

CONCLUSION

From the results discussed above we conclude that for the compounds with the general structure $D-CH_2-A$ ($A = 4\text{-cyanopyridinium}$) (Table 1) an intramolecular CT band can only be observed if the HOMO of the donor has a relatively high absolute value for its orbital coefficient at the carbon atom to which the $-CH_2-A$ group is attached.

Intramolecular CT bands, involving lower MO's of the donor, can be observed under the same conditions, at least if the energy of these orbitals is high enough to assure that the corresponding CT bands will not be obscured by the absorption of the separate D and A parts.

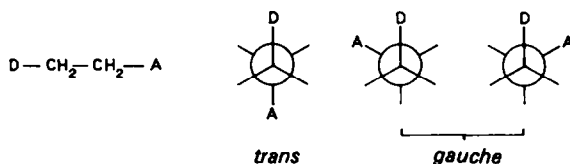
The dependence of the intramolecular CT transition on the value of the C_1 orbital

coefficient and the absence of this transition if the coefficient is zero, shows that a certain extent of overlap between the HOMO of the donor and the first vacant MO of the acceptor is an essential requirement for a CT transition to occur.

As we shall discuss in the theoretical part it may certainly not be assumed that the degree of overlap is the only factor governing the intensity of the CT transition. A simple relation between the C_1 orbital coefficient and the intensity of the intramolecular CT transition in compounds $D-CH_2-A$ with variable D and fixed A can therefore not be expected.

Two methylene groups between donor and acceptor. From the data collected in Tables 1 and 2 it follows that the position of the intramolecular CT band remains almost unchanged if the chain between D and A is lengthened from one- to two methylene groups. Compounds LXIII and LXXIV (involving 1,3,5-trimethoxybenzene as a donor) form a noteworthy exception.

In compounds with a chain of two methylene groups, D and A can occupy *gauche* positions allowing a stronger and less localized overlap between their π -electron systems than possible with a "chain" of one methylene group.



Nevertheless the condition that the HOMO of D must have a large orbital coefficient on the C atom with which it is attached to the chain, seems to hold for the compounds from Table 2 as well. For compound LXX only the CT band attributable to the HOMO of 1,3-dimethoxybenzene is observed, while for compound LXXII—involving the same donor linked to the chain at a different position—no CT band is observed, analogous to the results obtained for the lower homologues (LIX and LVIII) with one chain C atom less.

For steric reasons the *trans*-rotamer seems to be favoured over the *gauche*-rotamers in the compounds with a chain of two methylene groups. One might expect that for strong donors (e.g. 1,4-dimethoxybenzene or 1,2,4-trimethoxybenzene) the CT bonding energy between D and A will lower the energy of the *gauche*-rotamers, decreasing the average distance between D and A . For such strong donors a large intensity increase of the CT band would then be expected for the higher homologue (with C_2 -instead of C_1 -chain). The data from Tables 1 and 2 do *not* substantiate these expectations, and show that other factors are involved, which are discussed in a following paper.

Three or more methylene groups between donor and acceptor. As we have reported earlier,¹ the intensity of the intramolecular CT absorption in $D(CH_2)_nA$ declines rapidly if the length of the methylene chain is increased to three or more methylene groups. Even for a chain of three methylene groups ($n = 3$) no discrete CT maximum is normally observed. In compound LXXX with $n = 3$ and the strong donor 1,2,4-trimethoxybenzene a shoulder in the expected region can be observed (cf. Fig. 7) with $\epsilon_{405} \approx 195$.

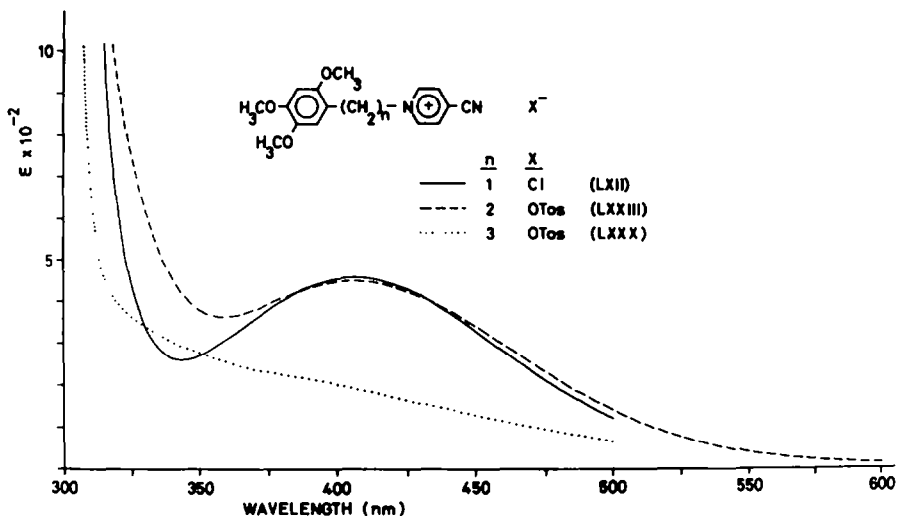


FIG. 8 Absorption spectra in ethanol (96%) of: LXII, LXXIII, and LXXX.

These weak intramolecular CT absorptions for compounds with $n > 2$ indicate that the heat of formation, for intramolecular complex formation between D and A, is too small to compensate the loss of entropy, caused by the restricted mobility of the methylene chain upon intramolecular complex formation. For a long methylene chain the interaction between D and A has the character of a "contact CT"²⁵ and thus will be comparable to that of weak intermolecular CT complexes.

THEORETICAL PART

The strong colour phenomena, observable in solutions containing mixtures of a compound with a low ionization potential and a compound with a high electron affinity, have led to an extensive investigation of the nature of the interaction between such compounds.

Mulliken's²⁶ theory of charge transfer (CT) forms the basis for our present understanding of these interactions. Mulliken considered the interaction of a no bond ground-state $\psi_0(D, A)$ and a polar excited state $\psi_1(D^+ - A^-)$ to produce a stabilized ground state:

$$\psi_0' = \psi_0(D, A) + \lambda\psi_1(D^+ - A^-)$$

$$\psi_1' = \psi_1(D^+ - A^-) + \mu\psi_0(D, A)$$

Since generally both λ and μ will be $\ll 1$, there is very little CT in the ground-state of the complex. Thus as pointed out by Murrell,²⁷ the expression CT-complex is quite meaningless. The description of the observed new absorption band—involving excitation from ψ_0' to ψ_1' —as a CT band however is very descriptive. Upon excitation of the complex in its CT band, a charge—which is close to unit—is transferred from D to A.

The degree of CT in the ground-state has been calculated from the dipole moment of CT complexes. It has however been shown recently that these calculations have strongly overestimated the degree of ground-state CT.²⁸ Especially Dewar²⁹ has

TABLE 5.

		C_s	C_s	C_{2v}
Energy (β)		-0.35331	-0.48623	-0.34072
Symmetry		A''	A''	$B_1 - S_z$
First vacant MO at various positions	Orbital coefficient			
	1	-0.35644	-0.36108	-0.34323
	2	+0.47158	+0.35870	+0.40170
	3	-0.06865	+0.18663	+0.20636
	4	-0.44733	-0.58716	-0.47201
	5	+0.22670	+0.09892	
	6	+0.36724	+0.53905	
	7	+0.28720	+0.15300	-0.27988
8	-0.42072	-0.19390	+0.41614	
Energy (β)		-0.81067	-0.71263	-1.00000
Symmetry		A''	A''	$A_2 - A_z$
Second vacant MO at various positions	Orbital coefficient			
	1	-0.14512	-0.15405	+0.00000
	2	-0.13501	+0.61153	-0.50000
	3	+0.54124	-0.28175	+0.50000
	4	-0.30376	-0.01446	-0.00000
	5	-0.29499	+0.29206	
	6	+0.54290	-0.19367	
	7	-0.31852	-0.44032	-0.00000
8	+0.30378	+0.45389	-0.00000	
Charge distribution				
Atom	2-cyano	Pyridinium-ion		4-cyano
		2-cyano	3-cyano	
1	+0.37099	+0.37934	+0.37934	+0.37912
2	+0.19681	+0.27289	+0.27289	+0.23682
3	+0.01910	-0.02109	-0.02109	+0.00258
4	+0.16112	+0.18046	+0.18046	+0.13890
5	-0.00082	-0.01388	-0.01388	+0.00258
6	+0.25140	+0.25267	+0.25267	+0.23682
7	+0.15983	+0.17290	+0.17290	+0.16747
8	-0.15843	-0.22329	-0.22329	-0.16427

TABLE 6. PARAMETERS USED IN THE HMO CALCULATIONS:

Atom	h	Bond	k
C	0	C...C	1.0
		C—C	0.9
		C=C	1.1
O	2.0	C—O	0.8
N	0.5	C...N	1.0
⊕		C≡N	1.25*
N	2.0		

* This value was derived from the assumed proportionality of k with the overlap integral³⁵ and a C≡N bond length of 1.16 Å. Our value is close to $k = 1.2$ used by Zweig *et al.* (ref. 36).

pointed out that the ground-state stabilization by charge resonance is probably of minor importance in many cases.

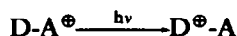
If the contribution of the polar state to the ground-state is very small (i.e. $\lambda \approx 0$) the difficulty arises to explain the rather great intensity of the observed CT bands, since it can be shown that for $\lambda = 0$ the intensity of the CT band will normally be very small. Murrell²⁷ has pointed out that this difficulty can be overcome by mixing of the CT state ($D^+ - A^-$) with locally excited states ($D - A^*$) and ($D^* - A$) in the donor or acceptor. Especially if the donor and/or acceptor show intense transitions at an energy close to that of the CT transition, this mixing of the CT state with the locally excited states can lead to an important "intensity borrowing" of the CT transition from the original transitions in D and A. Calculations by Iwata *et al.*³⁰ for complexes of various donors with tetracyanobenzene have shown the importance of this "intensity borrowing". Thus the intensity of CT bands is not necessarily zero if the overlap between the highest occupied molecular orbital of the donor and the first vacant orbital of the acceptor which governs λ , is zero. Complex configurations not fulfilling Mulliken's maximum overlap principle³¹ can therefore strongly contribute to the intensity of the observed CT bands. The energy of a CT transition is to a first approximation given by:

$$h\nu = I_D - E_A + C$$

in which I_D is the ionization potential of the donor, E_A the electron affinity of the acceptor and C the Coulomb interaction energy between D^+ and A^- .

From studies at high pressure³² it is known that $h\nu$ strongly depends on the distance between D and A, which is mainly caused by the Coulomb term $C = -e^2/r$.

For complexes in which the acceptor is a positive ion—as is the case for the pyridinium compounds studied by us—the CT transition is not accompanied by a charge separation but merely by a redistribution:



In this case the transition energy will be:

$$h\nu = I_D - E_A$$

For these complexes we can expect the energy of the CT transition to be rather insensitive for the distance between D and A[⊕], which seems to be substantiated by the insensitivity of the energy of the intramolecular CT transition for the length of the methylene chain which links D and A[⊕].

Appendix 1

Determination of ionization potentials. Voigt and Reid²⁴ have shown that an excellent linear relationship exists between the ionization potential—as measured by the photoionization method—of substituted benzene derivatives and the energy of the first CT transition of their complexes with tetracyanoethylene in dichloromethane as a solvent:

$$h\nu = 0.925 I_D - 5.12 \text{ (eV)}$$

Since no photoionization potentials are available for most of the donors used in the present study, we have calculated these via the relation of Voigt and Reid (cf. Table 3).

Appendix 2

Hückel calculations. To obtain a qualitative insight in the π -electron-distribution and energy of the D and A systems described in this paper, we have performed some simple Hückel LCAOMO calculations^{34, 35} In this method the introduction of heteroatoms is accounted for by adjustment of the Coulomb integrals (α_r) and the bond integrals (β_{rs}), with respect to the standard values (α and β) of benzene.

$$\alpha_r = \alpha + h_r \beta$$

$$\beta_{rs} = k_{rs} \beta$$

h_r and k_{rs} are parameters characteristic for the atoms (r and s) and the bonds between them.

As to the use of appropriate parameters great confusion seems to exist in the literature. This is because it is impossible to find parameters that can account simultaneously for all physical properties of a given molecule within the framework of the simple Hückel theory.

In our calculations we used exclusively standard parameter values as given by Streitwieser³⁴ (cf. Table 6). The influence of the alkyl groups was not accounted for, not in the methoxybenzenes, nor in the N-alkyl pyridinium ions. Our calculations for the methoxybenzenes (compiled in Table 4) are fully comparable with those of Zweig *et al.*,³³ who only gave the energies but not the coefficients of the MO's. For the different cyanopyridinium ions the results are compiled in Table 5. Taking the energy of the lowest vacant MO as a measure, the order of acceptor-strength is 4-cyano > 2-cyano > 3-cyano, which agrees with our previous experimental observations. Furthermore the energy separation between the lowest and second vacant MO decreases in the same order, which supports our explanation³ for the double CT band patterns observed in complexes of these ions with the iodide ion and in some cases with other donors as well.

EXPERIMENTAL

The UV and visible absorption spectra were measured with a Cary model 14 recording spectrophotometer in teflon stoppered silica cells of 1 cm pathlength. The position of the CT band maxima was determined from spectra scanned with a speed of 5 Å per sec; slower scanning yielding no improvement because of the broad shape of the bands.

N-[2-(*p*-anisyl)-1-ethyl]-4-cyanopyridinium chloride (LXVIII) was converted into the corresponding nitrate and sulphate by the following procedure: to an aqueous soln of LXVIII an equivalent amount of pure AgNO₃ or Ag₂SO₄ was added. The precipitated AgCl was then removed by filtration and after dilution the spectrum of the filtrate was measured. The synthesis of the compounds used in the present study has been described elsewhere.²

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