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STUDIES OF INTER- AND INTRA-MOLECULAR DONOR–ACCEPTOR INTERACTIONS—II[1,2]

INTERMOLECULAR CHARGE TRANSFER INVOLVING SUBSTITUTED PYRIDINIUM IONS

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Abstract—The intermolecular charge transfer (CT) interaction of various substituted aromatics and the iodide ion as donors, and substituted pyridinium ions as acceptors was studied. Relatively strong acceptor properties are displayed by the N-methyl-4-cyanopyridinium ion and with this ion a linear relationship is shown to exist between the ionization potential of the donor and the energy of the CT-transition as observed in the absorption spectrum. The complexes between N-methyl-4-cyanopyridinium ion and neutral aromatic organic donors are very weak as concluded from their equilibrium constants; the solvent dependence of the corresponding CT-bands cannot be correlated with solvent polarity parameters.

It is shown that the double CT-band pattern of many pyridinium iodides is probably caused by the presence of two closely located vacant molecular orbitals in the pyridinium ion.

INTRODUCTION

THE charge-transfer (CT) interaction between pyridinium ions and iodide ion has been studied extensively.[3] Qualitatively the relation between the biochemical importance of the nicotonamidium group and its electron acceptor properties has often been suggested.[4] Very few quantitative data, however, exist about the CT-interaction between pyridinium ions and neutral (aromatic) organic donors.

As part of a program, involving the study of inter- and especially intra-molecular donor–acceptor interaction,[1,2] we have studied the interaction of some substituted pyridinium ions with neutral (mostly aromatic) organic donors as well as with the iodide ion.

RESULTS AND DISCUSSION

CT-interaction of the 4-cyanopyridinium ion with some methoxy substituted benzene derivatives. From the N-alkylpyridinium ions (involving the 2,3 and 4-cyano ions), the 4-cyanopyridinium ion was found to display the strongest acceptor properties.

Ethanolic solutions, containing N-methyl-4-cyanopyridinium chloride and di-, tri- and tetra-methoxy substituted benzene derivatives, show "new" absorption bands in the visible or near UV region, which can be attributed to intermolecular CT-interaction.

If the interaction between an acceptor and a series of "related" donors is studied, a

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linear relation between the energy of the CT-transition (hν) and the ionization potential of the donor (I_D) is normally found.[5]

Graphical evaluation (Fig. 1) of the values from Table 1, shows that such a relation also holds very well for the interaction between methoxybenzenes and the N-methyl-4-cyanopyridinium ion.

TABLE 1. CT-ABSORPTION BANDS RESULTING FROM THE INTERACTION BETWEEN N-METHYL-4-CYANOPYRIDINIUM CHLORIDE AND SOME DONORS IN 96% ETHANOL

	I_D (eV)*	λ_{max} (nm)	$\tilde{\nu}_{max}$ (kK)	hν (eV)	$\Delta\tilde{\nu}_{\frac{1}{2}}$ (kK)†
1,4-Dimethoxybenzene	7·64	390 ± 0·5	25·64	3·18	3·61
1,3,5-Trimethoxybenzene	7·96	356·5	28·05	3·48	3·78
1,2,4-Trimethoxybenzene	7·49	405	24·69	3·06	3·90
1,2,3,5-Tetramethoxybenzene	7·25	433	23·09	2·86	3·86

* Ionization potentials were calculated by the method of Voigt and Reid,[5] from the CT-spectra of the donors with tetracyanoethylene in dichloromethane, employing the values from Ref. 5 for the CT-maxima, except for 1,2,4,5-tetramethoxybenzene for which 12·80 kK was found to be the correct position of its CT-band with TCNE.

† $\Delta\tilde{\nu}_{\frac{1}{2}}$ gives the difference in wavenumber between the maximum of the CT-band and the half-height position at the long wavelength side.

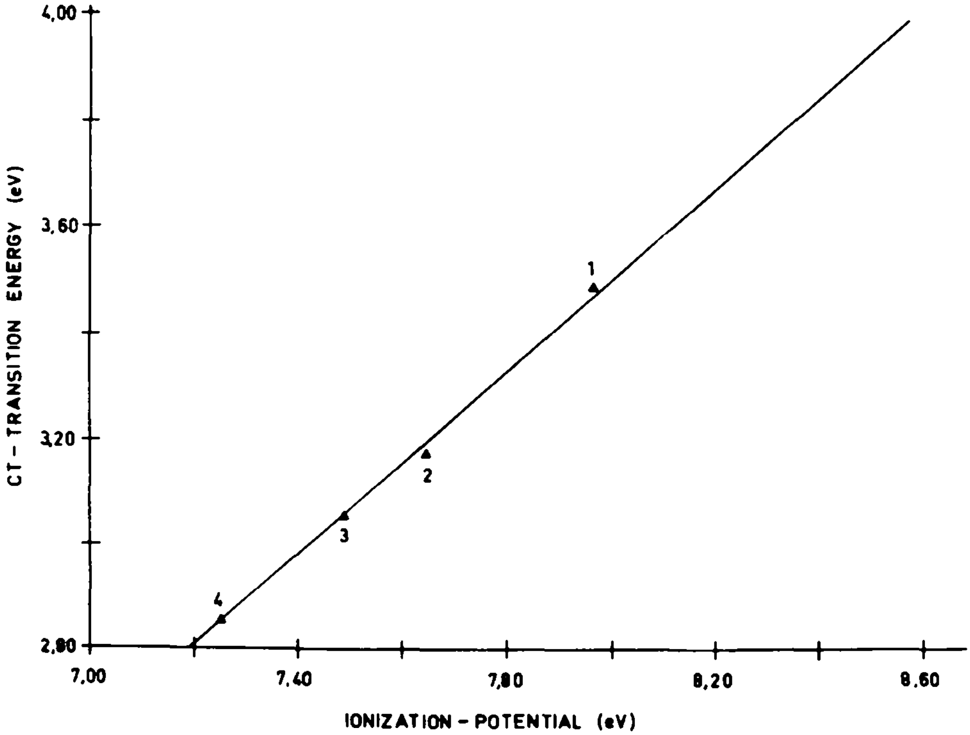

FIG. 1 Plot of the ionization potential (I_D) of some polymethoxy benzenes versus the energy of the intermolecular CT transitions resulting from their interaction with N-methyl-4-cyanopyridinium chloride in ethanol (96%). Substitution patterns: (1) 1,3,5; (2) 1,4; (3) 1,2,4; (4) 1,2,4,5. (cf. Table 1).

The relation evaluated by the method of the least squares is:

$$h\nu = 0{\cdot}87\, I_D - 3{\cdot}47\, (\text{eV}).$$

To investigate the molar ratio of donor and acceptor in the complexes, a Job plot[6] was evaluated for the system 1,4-dimethoxybenzene/N-methyl-4-cyanopyridinium chloride in ethanol. A series of solutions was made, containing a different ratio of donor (*D*) and acceptor (*A*), while the sum concentration of both was kept constant at 0·2M. A plot (Fig. 2) of the absorbance at some wavelengths in the CT-band *versus* the ratio of donor and acceptor gives a maximum at a 1 : 1 ratio. This, and the symmetry of the curves obtained, shows the composition of the donor-acceptor complex. No complications arise from the individual absorption of donor and acceptor, because the absorption of either is negligible at the wavelengths studied.

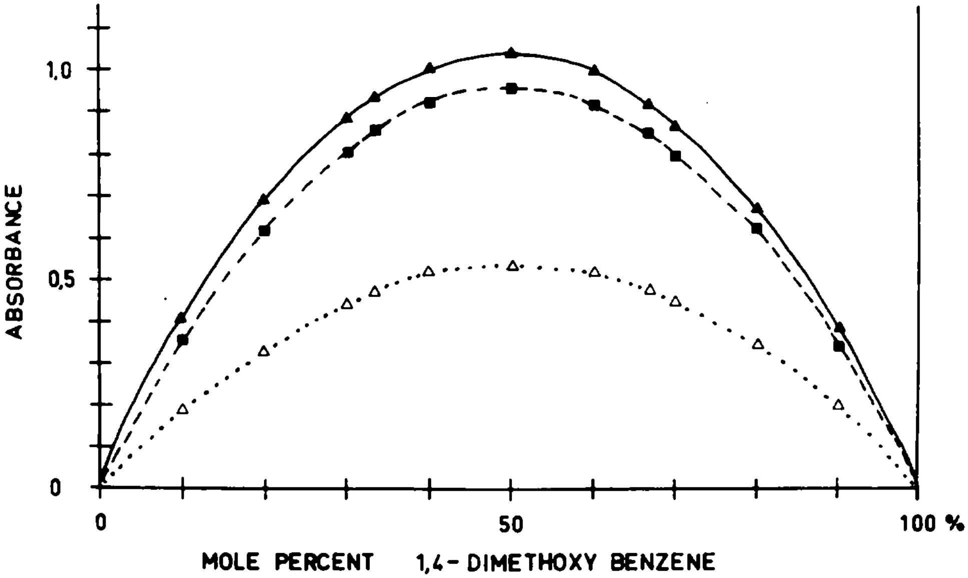

FIG. 2 Job plot for the system: 1,4-dimethoxy benzene/N-methyl-4-cyanopyridinium chloride (0·2M solutions in 96% ethanol). ▲ at 390 nm; ■ at 410 nm; △ at 450 nm.

For the complexes of 1,3,5-trimethoxy-; 1,4-dimethoxy- and 1,2,4-trimethoxybenzene with the N-methyl-4-cyanopyridinium ion, as well as for the complex of 1,4-dimethoxybenzene with the N-decyl-4-cyanopyridinium ion the equilibrium constant (*K*) and the molar extinction coefficient (ε) at some wavelengths (λ) were determined via the method of Benesi, *et al.*

To account for the weak nature of the complexes, the B.H.S.-equation was used in the following form:[7]

$$\frac{A_0 D_0}{E_\lambda} = \frac{1}{K\varepsilon_\lambda} + \frac{1}{\varepsilon_\lambda} D_0$$

A_0 and D_0 are the stoechiometric concentrations of acceptor and donor; E_λ is the optical density of the solution at wave-length λ for 1 cm pathlength. (The formula is valid only if $D_0 \gg A_0$ and if the donor and acceptor do not absorb in the region studied.)

A series of solutions was made with constant A_0 (A_0 = 0·005M with 1,3,5-trimethoxybenzene and 0·01M with the other donors) and D_0 varying from 0·1 to 1·0M.

Reasonable linear plots of A_0D_0/E_λ against D_0 were obtained.

From the slope (= $1/\varepsilon_\lambda$) and the intercept (= $1/K\varepsilon_\lambda$) both K and ε_λ were calculated at various wavelengths; the results are compiled in Table 2. From these figures it follows that: (i) the equilibrium constants found are rather small and in the order to be expected for a "pure" contact CT interaction,[9] (ii) the calculated equilibrium constants vary with the wavelength at which they are estimated and seem to decrease upon increasing wavelength. Since we have shown that the interaction is of the 1 : 1 type, this wavelength dependence of K is not due to the formation of higher order complexes.[8] Similar observations have been made before.[10]

TABLE 2. CALCULATED EQUILIBRIUM CONSTANTS (AT 25°), MOLAR EXTINCTION COEFFICIENTS (ε) AND THERMODYNAMIC PARAMETERS FOR COMPLEXES BETWEEN N-ALKYL-4-CYANOPYRIDINIUM IONS AND SOME METHOXYBENZENES IN 96% ETHANOL

Donor/Acceptor	λ* (nm)	ε	K 25° (l. mol^{-1})	ΔG 25° (kcal. mol^{-1})	ΔH (kcal. mol^{-1})	ΔS (cal. gr.$^{-1}$ mol^{-1})
1,4-Dimethoxybenzene/	360	258	0·390			
N-*methyl*-4-cyanopyridinium	$\underline{390}$	337	0·332	−1·03	−1·46	−143
ion	410	349	0·295			
	450	235	0·244			
1,3,5-Trimethoxybenzene/	$\underline{356}$	976	0·326	−1·02	−1·13	−107
N-*methyl*-4-cyanopyridinium	390	994	0·246			
..ion	420	727	0·172			
1,2,4-Trimethoxybenzene/	$\underline{405}$	575	0·243	−0·85	−1·66	−812
N-*methyl*-4-cyanopyridinium	450	521	0·209			
ion						
1,4-Dimethoxybenzene/						
N-*decyl*-4-cyanopyridinium	$\underline{390}$	340	0·330	−1·03	−1·46	−143
ion						

* λ_{max} has been underlined.

The apparent wavelength dependence of K may be explained from the observation, that the position of the intermolecular CT band depends on the concentration D_0. For the system N-methyl-4-cyanopyridinium chloride/1,4-dimethoxybenzene, a decrease of D_0 from 1·0M to 0·1M (A_0 = 0·01M) results in a shift of the CT band from 392·5 nm towards 389·5 ± 0·5 nm.

Such a hypsochromic shift will cause the absorption at the long wavelength side of the band to decline faster upon dilution than at the short wavelength side, so the calculated K's will decrease with increasing wavelength. Therefore the most reliable value of K will be the value estimated at λ_{max}. The band shift is surely due to the high concentration of the donor, which modifies the polarity of the medium. Since high donor concentrations are usually employed in evaluating K by the B.H.S. method, shifts due to this concentration effect may explain the apparent wavelength dependence of K in other cases as well.

From K the free enthalpy (ΔG) for formation of the complexes was calculated, through $\Delta G = -RT(\ln K - \ln V_0)$, V_0 is the molar volume of the solvent.

From the temperature dependence of K (range studied 25–55°) the heat of formation (ΔH) and the entropy (ΔS) were calculated. From the (negative) values of ΔH (cf Table 2) it can be concluded that the complexes are weak but not purely of the contact-CT type, since than $\Delta H \geqslant 0$ should be found. The formation entropies are negative too, showing that complex formation decreases the disorder of the system.

It is interesting to note that the thermodynamic parameters of complex formation are independent on the size of the N-alkyl substituent as is shown by comparison of N-methyl- and N-decyl-4-cyanopyridinium ion. This observation indicates that the configuration of the intermolecular complex is such that the N-alkyl group does not hinder the mutual approach of the donor and the acceptor. A model in which the planes of the donor and acceptor are plane-parallel, giving maximum overlap of both π-electron systems, will fulfil this condition.

Influence of ring-substituents on the acceptor properties of the N-*methylpyridinium ion.* From the substituted N-methylpyridinium ions, tabulated in Table 3, the CT spectra with the iodide ion, with 1,2,4,5-tetramethoxybenzene and with N,N-dimethylaniline were measured. The figures from Table 3 show, that the order of acceptor strength is independent of the donor employed. Judging from the wavelength of the first CT band, the N-methyl-4-cyanopyridinium ion displays the strongest acceptor properties.

TABLE 3. POSITION OF THE CT-BANDS FROM VARIOUS SUBSTITUTED N-METHYL-PYRIDINIUM IONS WITH SOME DONORS

N-methyl-pyridinium ion	Donor		
	I^{-} ion in acetone	1,2,4,5-Tetra methoxybenzene in 96% ethanol	N,N-Dimethyl aniline in 96% ethanol
4-Cyano	464; 322 nm	433 nm	473 nm
2-Cyano	453; 336	(395)	448
3-Cyano	(420); 362·5	—	(430); 361
4-Amido	384	(380)	421

( ) = shoulder

The spectra of pyridinium iodides often show two CT bands. Kosower c.s.[11] attributed these bands to the formation of an iodine atome in the ${}^2P_{\frac{1}{2}}$ or ${}^2P_{\frac{3}{2}}$ state upon excitation of a pyridinium iodide in the first and the second CT band respectively.

$$\mathrm{Py}^{+}\,\mathrm{I}^{-} \longrightarrow \mathrm{Py}^{\bullet}\,\mathrm{I}^{\bullet}$$

This explanation seems to be supported by the separation between the two CT bands for N-methylpyridinium iodide, which is almost equal to the energy difference between the $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states of the iodine atom.

It, however, has been observed before,[11] that upon introduction of substituents in the pyridinium ring (c.f. Table 3) the separation between the two bands varies strongly.

Introduction of an electron withdrawing substituent at the 4-position strongly increases the separation, while such a substituent at the 3-position brings the bands very close together.

Furthermore the CT spectrum of the N-methyl-3-cyanopyridinium ion with N,N-dimethylaniline also shows a double band pattern, with approximately the same band separation as in the spectrum of N-methyl-3-cyanopyridinium iodide (c.f. Fig. 3 and Fig. 4).

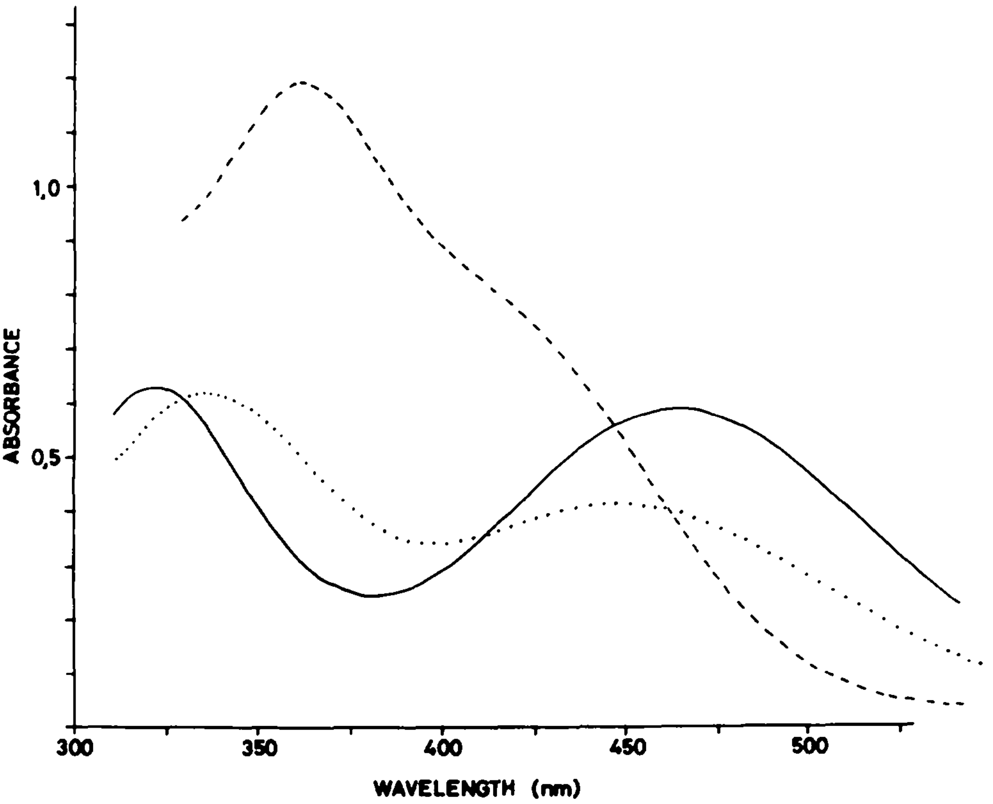

FIG. 3 CT spectra of cyano-substituted N-methyl pyridinium iodides in acetone (0·002M solutions).
——— 4-cyano; ---- 3-cyano; .... 2-cyano.

It seems possible that the N-methyl-4-cyanopyridinium ion and the N-methyl-2-cyanopryidinium ion give a second CT band with N,N-dimethylaniline, which is obscured by the absorption of N,N-dimethylaniline itself.

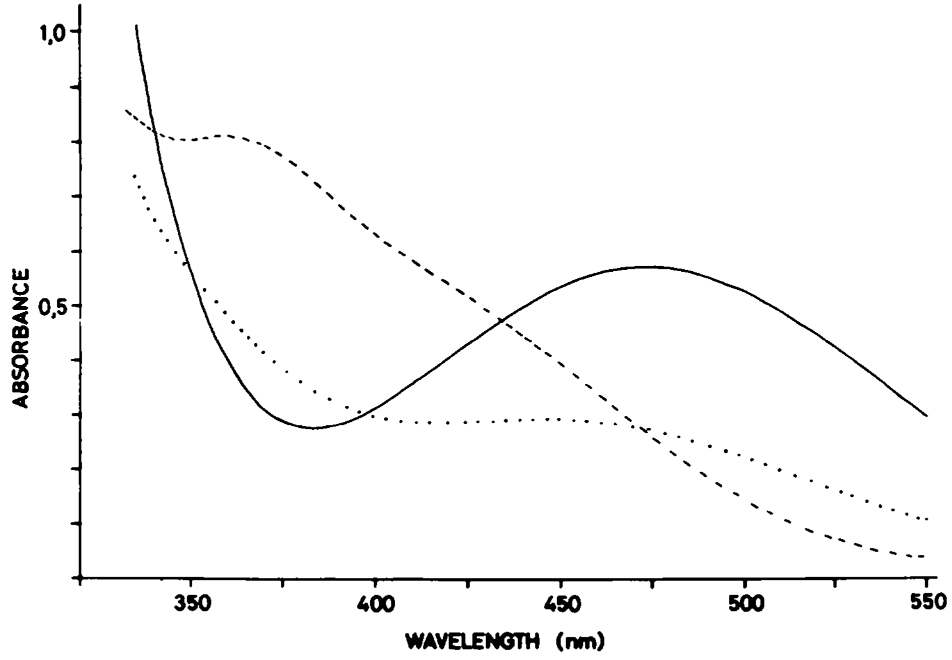

Fig. 4 CT spectra resulting from the interaction of N,N-dimethyl-aniline (0·2M) with cyano-substituted N-methyl pyridinium ions (0·01M) in 96% ethanol.
——— 4-cyano; ---- 3-cyano; .... 2-cyano.

In our opinion the occurrence of two CT bands is due to the presence of two vacant molecular orbitals in the pyridinium ion, the energy difference between those M.O.'s governing the separation of the CT bands. Such an explanation for a double CT band pattern has recently been given[12] for complexes involving 1,2,4,5-tetracyanobenzene as an acceptor.

The N-methylpyridinium ion has C_{2v} symmetry. The lowest vacant orbital will belong to the B_1 species and the second vacant orbital to the A_2 species.[13] The second vacant orbital will have a nodal plane through the N atom and the C-4 atom, perpendicular to the plane of the ring. Introduction of an electron withdrawing substituent at C-4 will mainly lower the first vacant orbitals energy, increasing the separation between the two CT bands. Introduction of such a substituent at C-3 or 2 however, will influence both vacant orbitals. Under the simplified assumption, that the position of the CT bands is only determined by the energy separation between the highest occupied M.O. of the donor (i.e. the I^- ion) and the appropriate vacant orbital of the acceptor (i.e. the pyridinium ion), it is possible to calculate the *relative* energies of the first vacant orbitals in the N-methylpyridinium ions from the CT-transition energies. In Fig. 5 this is demonstrated for N-methylpyridinium iodide and its cyano-substituted derivatives in acetone. (The position of the two CT bands of N-methylpyridinium iodide in acetone was calculated from the values in chloroform and the Z values of chloroform and acetone resp.[3])

In principle the present explanation for the double CT band pattern is analogous to the one given for the double band pattern observed for CT interaction between dimethoxybenzenes and tetracyanoethylene.[5] The latter is explained by the existence of two closely located *occupied* M.O.'s in the donor, the separation of which decreases in the order 1,4 → 1,2 → 1,3-dimethoxybenzene.

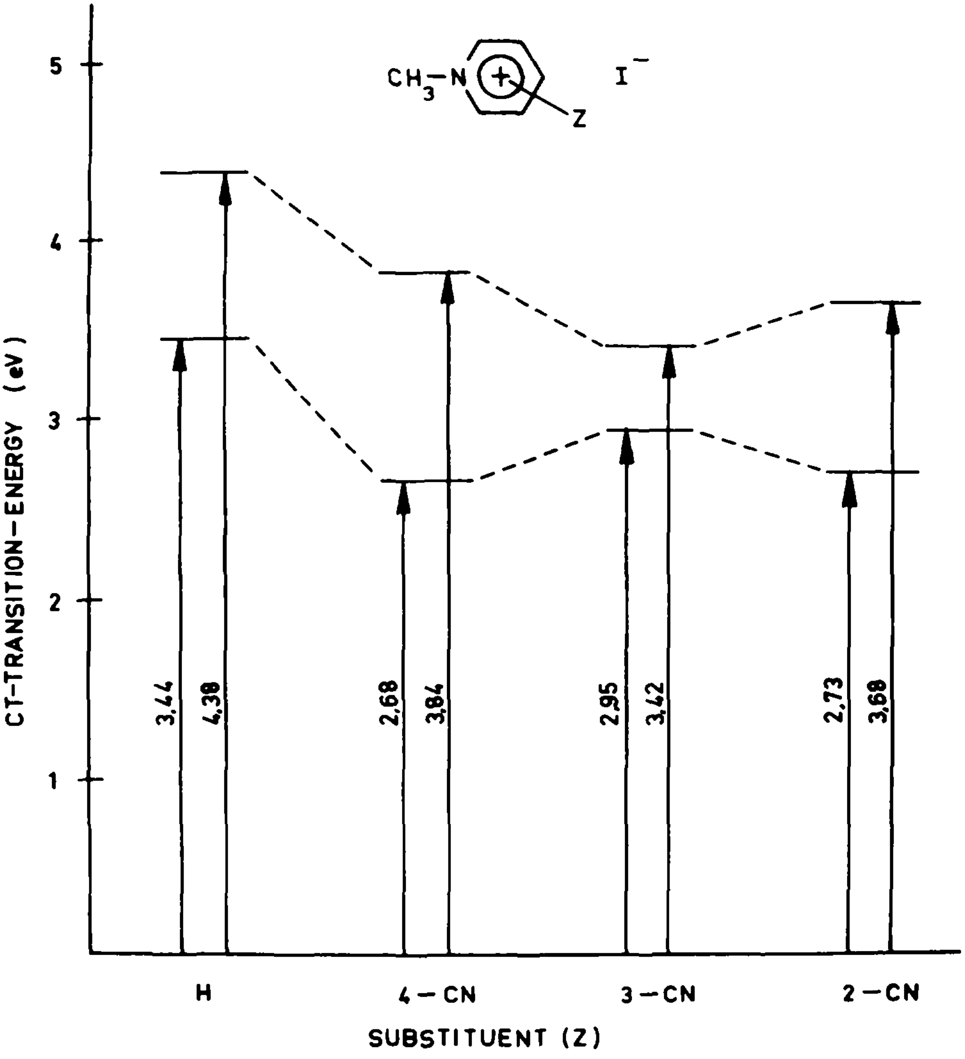

Fig. 5 Relative energies (eV) of the lowest two unoccupied molecular orbitals in N-methyl pyridinium ions, as reflected in the energy of CT transitions in the corresponding pyridinium iodides.

Influence of the N-*substituent on the acceptor properties of the* 4-*cyanopyridinium ion.* For a series of N-substituted 4-cyanopyridinium ions, the CT interaction was measured with three donors i.e. the I^- ion, 1,2,4,5-tetramethoxybenzene and N,N-dimethylaniline. Results—compiled in Table 4—show that introduction of various primary alkyl groups has very little influence, which agrees with the relevant literature.[3]

TABLE 4. POSITION OF THE CT-BANDS FROM VARIOUS N-SUBSTITUTED-4-CYANOPYRIDINIUM IONS WITH SOME DONORS

R	Donor		
	I^- Ion in acetone	1,2,4,5-Tetra methoxybenzene in 96% ethanol	N,N-Dimethyl aniline in 96% ethanol
Methyl	464 nm	433 nm	473 nm
n-Butyl	461	432·5	473
n-Decyl	461	433	473
4-NO_2-benzyl	468	—	486
3-NO_2-benzyl	467	—	484
4-Cl-benzyl	466	444	487·5
benzyl	467·5	442·5	487
4-Me-benzyl	466	438	483
4-MeO-benzyl	464·5	—	482
2-Phenylethyl	465	437	479
3-Phenylpropyl	459	433	473
4-Phenylbutyl	460	433	474

The influence of a N-benzyl group and substituents therein has been studied for N-benzyl-4-carbomethoxypyridinium iodide in *cis*-1,2-dichloroethylene.[14]

The frequency of the CT band was found to be linearly related to the Hammett σ constant of the substituents in the benzyl group. For our system we were unable to reproduce these results; the effect of substituting N-benzyl for N-alkyl is small and the effect of substituents in the benzyl group is very small, though there is some trend in the expected direction. This different behaviour may be caused by the difference in solvents used (the pyridinium iodides studied here are insoluble in *cis*-1,2-dichloroethylene). Since CT bands of pyridinium iodides are extremely sensitive for changes in medium polarity and polarity changes, if caused by substituents in the benzyl group, may be much more effectively transmitted by one solvent than by another.

With the neutral donors, substitution of N-alkyl by N-benzyl has a stronger effect. Substituents in the benzyl group have a small effect. From 4-methoxybenzyl to 4-chlorobenzyl the wavelength of the CT band increases as expected from the increasing electron attracting properties of the substituent. For 3- and 4-NO_2-benzyl the wavelength decreases markedly. In these cases we must consider the molecule to have two acceptor sites; the pyridinium ring at one side, the nitrophenyl system at the other. Competition between these two acceptor sites seems to hinder specific complex formation with one of them. With tetramethoxybenzene as a donor no discrete CT maxima for the nitrosubstituted systems could be detected, possibly as a result of overlap between the CT band with the pyridinium part and with the nitrophenyl part.

Upon lengthening of the methylene chain between them, the effect of the phenyl group on the pyridinium group decreases sharply. From the small substituent effect in the benzyl substituted compounds one may conclude that even one methylene group is an effective isolator for the mesomeric or inductive interaction between both aromatic systems. Whether the remaining interaction is largely transmitted through space or through the chain cannot be said with certainty.

Influence of the solvent on the position of the CT band. The solvent sensitivity of the CT band in pyridinium iodides is well known and the position of the first CT band for N-ethyl-4-carbomethoxypyridinium iodide (in kcal/mol) is used as a measure for solvent polarity (Z value).[15]

This strong solvent effect can be explained by the essential ion pair character of ground state and the apolar character of the excited state in pyridinium iodides; polar solvents will stabilize the ground state and produce a hypsochromic shift of the CT band.

For complexes of pyridinium ions with neutral donors however, the situation is more complex and in fact no simple relation between the position of the CT band and common solvent polarity parameters has been found in related cases.[16, 17]

$$\mathrm{Py}^+ D \rightarrow \mathrm{Py}^{\cdot} D^+$$

Upon excitation a positive charge is displaced from the pyridinium ion towards the donor. Since the solvent molecules do not change their position during the excitation (Franck Condon principle), one may expect that in solvents with a high *permanent* dipole moment (e.g. dimethylsulphoxide, dimethylformamide, acetonitrile) the ground state will be more stabilized than the excited state, which will result in a CT

TABLE 5. POSITIONS OF THE CT-BAND FROM N,N-DIMETHYLANILINE WITH N-(n-DECYL)-4-CYANOPYRIDINIUM *p*-TOLUENESULPHONATE IN VARIOUS SOLVENTS

Solvent	λ_{max}(nm)	$\tilde{\nu}_{max}$(kK)	Z (kcal. mol^{-1})*	D.C.*
Ethyleneglycol	470·0 ± 0·5	21·28	85·1	37·7
Methanol	468	21·37	83·6	32·6
Ethanol (100%)	472	21·19	79·6	24·3
Ethanol (96%)	473	21·14	—	—
n-Propanol	472	21·19	78·3	19·7
n-Butanol	471	21·23	77·7	17·7
Iso-propanol	467·5	21·39	76·3	18·3
t.-Butanol	456	21·93	71·3	12·2
Acetonitrile	462·5	21·62	71·3	37·3
D.M.S.O.	444	22·52	71·1	48·9
D.M.F.	445	22·47	68·5	36·71
Acetone	451·5	22·15	65·7	17·4
Dichloormethane	480	20·83	64·2	8·4
Chloroform	475·5	21·03	63·2	4·7
1,2-Dimethoxyethane	438·5	22·80	62·1	3·5–6·8

* Z-values and dielectric constants of the solvents from Ref. 18.

band at short wavelength. Our measurements for the system N,N-dimethylaniline/ N-decyl-4-cyanopyridinium *p*-toluenesulphonate (c.f. Table 5) do substantiate this. (The N-decyl salt was chosen for its solubility in a variety of solvents).

Stabilization of the excited state can occur by induced dipole interaction in polarizable solvents. In less polar solvents ion pair formation will be come increasingly important. The vicinity of the anion will lower the acceptor properties of the pyridinium ion,[17] which may explain the short wavelength in 1,2-dimethoxyethane.

EXPERIMENTAL

Most UV spectra were obtained with a Cary model 14 recording spectrophotometer at room temp in teflon stoppered silica cells of 1 cm pathlength.

Measurements for the evaluation of thermodynamic complex parameters were accomplished with a Zeiss PMQ II spectrophotometer, equipped with a thermostable cell jacket.

Interaction of the iodide ion with various pyridinium ions was measured in solns of the appropriate pyridinium iodide (0·002M) in dry acetone (below 340 nm 1 mm cells were employed).

Interaction of the various pyridinium ions with neutral donors was measured by addition of the donor to a soln of the appropriate pyridinium chloride or -*p*-toluenesulphonate.

Commercially available solvents were of purest grade and were dried over molecular sieves and distilled before use.

The synthesis of the pyridinium salts has been described elsewhere.[2]

N,N-dimethylaniline was distilled from calciumhydride and stored in a refrigerator under nitrogen atmosphere.

Anisole, all dimethoxybenzenes and 1,2,4-trimethoxybenzene were obtained from Fluka; 1,3,5-trimethoxybenzene from Columbia.

1,2,4,5-Tetramethoxybenzene was synthesized from *p*-benzochinon by the method of Bennington.[19] The crude product was recrystallized from cyclohexane, m.p. 102–103°.

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