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CHARGE-TRANSFER COMPLEXES IN ORGANIC CHEMISTRY—XII

SOLVENT EFFECTS ON CHARGE-TRANSFER SPECTRA[1]

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Abstract—The charge-transfer transition energies of 2,6-dimethoxynaphthalene and 9-methylanthracene with tetrachlorophthalic anhydride, and acenaphthene and anthracene with 3,5-dinitrophthalic anhydride were measured in sixty aprotic solvents. The observed effects can be interpreted in terms of various solvent parameters if the solvents are divided into the following classes: halogen-containing, aromatic and n-donor solvents.

In the present work we extend our solvent effect studies on charge transfer spectra in order to confirm and generalize our previous results.[2] Hildebrand *et al.* have pointed out that aromatic solvents give a different straight line than the halogen containing solvents, when the charge-transfer absorption maxima of the complex solvent-iodine is plotted against the ionization potential (I_D) of the solvents.[4] Later it was recognized that n-donor molecules give another relation for the same type of plot.[3] The more complete work of Voigt showed finally the following classes: alkanes, alkyl halides, aromatics, oxygen compounds, sulphur compounds and nitrogen compounds.[33,34]

It seems that similar differentiation occurs when one CT complex is examined in different solvents.[2] Voigt[5] found that hydrocarbons and perfluorohydrocarbons form two different classes, when the charge-transfer maxima of several complexes aromatics-tetracyanoethylene (TCNE) are plotted vs the polarizability parameter $(n^2-1)/(2n^2+1)$, n being the refractive index. Foster and Emslie had to distinguish between two type of solvents, protic (alcohols) and aprotic ones (chlorine-containing, hydrocarbon).[6] Ilmet and Berger[7] have also emphasized that aromatic solvents did not follow the relationship λ_{max}/n for the complexes of aromatic donors with 3-nitro-1,8-naphthalic dianhydride and 1,4,5,8-naphthalene tetracarboxylic dianhydride. Special effects due to aromatic solvents were invoked. (Let us notice that the theoretically correct relationship should be $\bar{\nu}_{max}$ vs $(n^2-1)/(2n^2+1)$, where $\bar{\nu}_{max}$ is the wave number in cm^{-1}; nevertheless the conclusion of the authors remains true).

We have found in the case of the complex acenaphthene (ACE)-tetrachlorophthalic anhydride (TCPA) that different classes of solvents must be distinguished in order to understand the solvent effect on the absorption spectra: chlorine-containing (class a), aromatic (class b) solvents which influence the charge-transfer absorption band mainly by general polarity-polarizability effect, while the n-donor solvents (class d in Ref 2) are acting mainly by their free electron pair. A theoretical explanation was proposed for the latter class. The aromatic solvents containing "one functional" group could not be classified clearly (class c in Ref 2).

In order to check the validity of the interpretation and the validity of the proposed classification we have extended the study to the complexes 2,6-dimethoxynaphthalene (2,6DMON)-TCPA, 9-methylanthracene (9MANT)-TCPA, ACE-3,5-dinitrophthalic anhydride (3,5DNPA) and anthracene (ANT)-3,5DNPA. We also include a review of the limited literature data.

We have found that the interpretation previously given[2] is fully satisfied, but the classification of the solvents into the above mentioned classes must be modified. This conclusion emphasizes further that specific solvent effects do play a great rôle at least in the case of complexes where the excited state, is more polar than the ground state.

RESULTS AND DISCUSSION

The spectroscopic data of the four complexes are reported in Table 1. The stoichiometry of the complex ACE-3, 5DNPA was established as 1:1,[8] and that of the other complexes was assumed to be 1:1 on the basis of the results obtained with similar donors.[8,9]

$\bar{\nu}_{max}$ did not follow the theoretical $(\epsilon_0-1)/(2\epsilon_0+1)$ parameter[10] (ϵ_0 is the dielectric constant) of polarity, neither did the polarisability parameter $(n^2-1)/(2n^2+1)$.[10]

At present only empirical parameters, such as the Z†,[11,15] E_T‡[12,13] of S_M[14] values are convenient to character-

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† Z value is the energy of the intermolecular charge-transfer in kcal mol^{-1} of 1-ethyl-4-carbomethoxypyridinium iodide at 25°C.

‡ E_T value is the energy, in kcal mol^{-1}, of the intramolecular charge-transfer band of pentaphenyl pyridinium-N-phenol betaine at 25°C.

Table 1. Spectroscopic data of the complexes in different solvents at 20°C

N°	Solvent	$5 + S_M$[a]	$\Delta\bar{\nu}_D$[b] (cm^{-1})	ACE-3, 5DNPA $\bar{\nu}_{max}$ (kK)	ACE-3, 5DNPA $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ (cm^{-1})	ANT-3, 5DNPA $\bar{\nu}_{max}$ (kK)	ANT-3, 5DNPA $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ (cm^{-1})	9MANT-TCPA $\bar{\nu}_{max}$ (kK)	9MANT-TCPA $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ (cm^{-1})	2,6DMON-TCPA $\bar{\nu}_{max}$ (kK)	2,6DMON-TCPA $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ (cm^{-1})
Class (a)											
1	n-Chlorobutane	3·114	—	21·10	2300	—	—	—	—	24·7	—
2	Dichloromethane	4·447	−12	20·35	2400	18·45	2200	21·7	2100	23·2	2450
3	Chloroform	4·114	−17	20·2	2300	18·25	2300	21·5	2100	23·1	2500
4	Carbon tetrachloride	2·146	−21	20·75	2100	18·6	1750	21·7	1700	23·3	2400
5	1,2-Dichloro ethane	4·580	2	20·6	2400	18·6	2300	21·8	2200	23·2	2450
6	1,1-Dichloro ethane	3·914	—	20·85	2450	19·0	2500	22·0	—	23·4	2400
7	1,1,2,2-Tetra chloroethane	4·940	—	20·2	2450	18·1	2450	21·4	2250	22·95	2500
8	Pentachloroéthane	3·547	—	20·35	2250	18·2	2000	21·6	2200	23·1	2400
9	1,2,3-Trichloropropane	4·643[c]	—	20·2	2350	18·25	2200	21·55	2500	23·1	2450
10	n-Chlorohexane	3·869	—	—	—	—	—	22·25	—	23·4	2500
11	Chlorocyclohexane	2·892[c]	—	21·05	2200	19·05	2300	22·1	2750	23·3	2400
12	Dichloro ethylene trans	2·477	—	20·5	2150	18·5	2000	—	—	23·2	2450
13	1,1-Dichloro ethylene	2·732[c]	—	—	—	—	—	21·8	1800	23·35	—
14	Trichloroethylene	2·973	—	20·4	2150	18·4	1750	—	—	—	—
15	Tetrachloroethylene	1·778	—	20·65	2100	—	—	21·9	2200	23·1	2200
16	t-Butylbromide	2·987[c]	—	21·1	2350	19·05	2250	—	—	—	—
Class (b)											
17	Benzene	3·255	0	20·4	2200	18·5	2100	21·9	2100	23·25	2450
18	Toluene	2·978	2	20·5	2200	18·6	2100	22·05	2250	23·3	2300
19	m-Xylene	2·716	—	20·6	2250	18·6	2050	22·11	2000	23·4	2300
20	p-Xylene	2·740	—	—	—	18·6	2050	22·05	2400	23·5	2500
21	Mesitylene	2·380	—	—	—	—	—	22·2	2000	—	—
22	Ethylbenzene	2·845	4	20·5	2200	18·6	2150	21·9	2300	23·3	2300
23	Chlorobenzene	3·845	−2	20·35	2300	18·4	2150	—	—	—	—
24	Bromobenzene	3·949[c]	−1	20·4	2300	18·4	2300	21·8	2200	23·05	2300
25	Benzylchloride	4·369[c]	—	20·25	—	18·4	2400	21·65	2600	23·0	2400
26	o-Dichlorobenzene	4·000	−11	—	—	—	—	21·55	2300	23·0	2400
Class (c)											
27	Benzaldehyde	4·556	53	21·1	2800	19·0	2500	21·75	2250	23·1	2500
28	Nitrobenzene	4·681	21	—	—	18·75	2350	—	—	—	—
29	Propionaldehyde	—	85	22·25	3150	19·8	2500	22·6	2400	23·8	—
30	Butyraldehyde	—	83	—	—	20·05	2650	22·6	—	23·8	2400
31	Crotonaldehyde	—	75	—	—	—	—	22·35	2600	23·7	2500
32	Valeraldehyde	—	—	—	—	—	—	22·4	—	23·8	—
33	Caproic aldehyde	—	—	—	—	—	—	—	—	23·6	2400
34	Methylacetate	—	36	22·3	3150	19·9	2650	22·0	—	23·7	—
35	Ethylacetate	3·343	39	21·9	2700	20·05	2850	—	—	23·75	—
36	Isobutylacetate	—	—	22·0	2650	19·95	2600	22·4	—	23·8	—
37	n-Butylacetate	2·653	—	—	—	—	—	22·4	—	23·8	2400

38	Isopropylacetate	—	—	—	—	—	—	22·55	2250	23·8	—
39	Diethylether	2·079	78	21·3	2300	—	—	—	—	—	—
40	Dibutylether	1·600	—	21·2	2250	19·25	2250	—	—	—	—
41	1,2-Dimethoxyethane	3·435[c]	71	—	—	—	—	—	—	23·7	2600
42	Tetrahydrofuran	3·462	90	—	—	20·35	2800	22·7	2300	23·8	2600
43	2-Methyltetrahydrofuran	—	—	—	—	—	—	22·6	2400	23·85	—
44	Tetrahydropyran	—	93	22·6	3250	19·65	2550	—	—	—	—
45	1,4-Dioxan	3·568	77	21·45	2650	19·2	2350	22·3	2150	23·5	2500
46	Acetonitrile	4·670	49	—	—	20·2	3000	—	—	23·7	—
47	Capronitrile	4·079	—	—	—	19·95	2750	—	—	—	—
48	Nitromethane	5·040	6	21·4	2900	19·4	2550	21·7	2500	23·5	—
49	2-Nitropropane	—	—	21·65	2850	19·7	2600	—	—	—	—
50	Acetone	4·176	64	—	—	20·35	2800	—	—	23·8	2900
51	Acetophenone	4·623	56	—	—	19·2	2450	—	—	—	—
52	Cyclohexanone	4·204	66	—	—	20·15	3200	—	—	—	—
53	Dimethylformamide	5·778	107	—	—	—	—	22·75	2550	24·0	2700
54	NN'Dimethylacetamide	4·6[d]	113	21·0	—	19·65	2600	22·9	2600	—	—
55	Dimethylsulfoxide	5·204	141	—	—	—	—	—	—	24·0	2900
56	Benzonitrile	4·591	38	21·3	2800	19·1	2500	21·9	2350	23·25	2500
Miscellaneous											
57	n-Pentane	—	—	21·3	2350	—	—	—	—	—	—
58	Cyclohexane	0·845	—	21·05	1800	19·1	2150	21·2	—	—	—
59	Cyclohexene	1·301	—	20·9	2000	18·8	1850	—	—	23·2	—
60	Carbon disulphide	2·398	—	20·3	2050	18·4	2150	20·8	1600	—	—

[a] Refs 14, 25 and 26.

[b] Ref 30.

[c] G. Berrebi, Thèse de doctorat, Louvain, 1970.

[d] Estimated value from the E_T/S_M correlation (as a proof, see Ref 1, where 41 was estimated as 3.5).

ize the variation of $\bar{\nu}_{max}$ of a complex. These parameters include both the polarity and the polarizability factor.

S_M is defined as log k_2, where k_2 is the second order rate constant of the reaction of tri(n-propyl)amine with methyliodide.[2,14] This parameter is used because of the great number of solvents available. Let us note that all these three solvent parameters vary in parallel with each other.

Fig 1 shows the variation of $\bar{\nu}_{max}$ with S_M for the complex .ACE-3,5DNPA in the halogen (chlorine)-containing solvents. There is a red shift with increasing polarity. It can be seen that two classes must be distinguished in these solvents: the per- or polyhalogenated solvents and those which are monohalogenated solvents or with few halogen substituents. In the former case, $\bar{\nu}_{max}$ varies less with S_M, there is a sort of "saturation effect", while in the latter case, the variation of $\bar{\nu}_{max}$ is more pronounced.[*] Similar variations can be found for the three other complexes. Thus the phenomenon must be rather general.

Voigt's results of the complex p-dimethoxybenzene-TCNE show similar splitting into two classes of the halogen-containing solvents (only $\bar{\nu}_{1/2}$ values are reported, because of the very large absorption maxima; a non-dependence of $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ with solvent is assumed).[16]

We have reported in Fig 2 the variation of $\bar{\nu}_{max}$ vs S_M in the aromatic solvents for the same complex. We can see the bathochromic shift with increasing polarity, as may be expected when the ground state is less polar than the excited state.[2] The same relation holds for the other three complexes. Chlorobenzene,[23] bromobenzene,[24] benzyl chloride,[25] and o-dichlorobenzene[26] follow the aromatic solvents as well as cyclohexane[58] and cyclohexene.[†][59] The sensitivity of $\bar{\nu}_{max}$ vs S_M is given by the slope of the straight lines (Table 2). They were calculated with $\bar{\nu}_{max}$ and S_M expressed in kcal mol^{-1} units and finally standardized against the Z values (in kcal mol^{-1}), using the known slopes of the relationships E_T/S_M (1·62) and Z/E_T (1·37).[15]

We have chosen the Z values as reference, because they represent the "maximum" solvent effect at present. This is a particular case where the ground state is very polar and the excited state is much less polar. The dipole moment of the complex not only diminishes when going from the ground to the excited state, but it also changes direction (approximately 90°). These two effects make the solvent effect very large.[15] (However the slope of $\bar{\nu}_{max}$ in kcal mol^{-1} of the charge-transfer maxima of tropylium iodide vs Z is 1·05, which casts doubt on the effect of the change in direction of the dipole in the reference pyridinium ion.[17])

The slopes $\bar{\nu}_{max}/Z$ show that the solvent effect is the greatest in the halogenated solvents (slope ~0·4), smaller in the aromatic solvents (slope ~0·3) and the smallest in the per- or polyhalogenated solvents (slope ~0·2). The variation of $\bar{\nu}_{max}$ in the case of complexes where the ground state is less polar than the excited state, is much less than in the opposite case (Z value). While for the iodide-pyridium complex[11,15] the polar and polarisability effects overshadow the small specific effects, in our case these latter effects do separate the solvents into different classes. The available literature data confirms this statement. However it must be emphasized that a small number of solvents studied can lead to an erroneous conclusion. The slope $\bar{\nu}_{max}$ vs Z is positive for the complex HEB,[‡][19,20] which would indicate that the complex is more

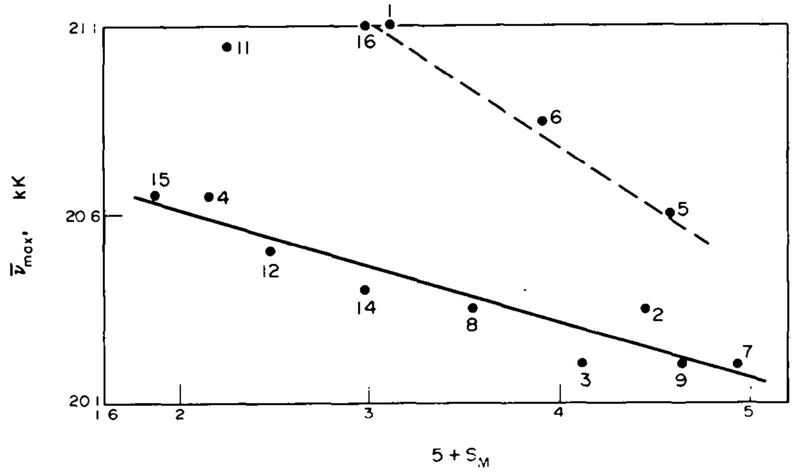

Figure 1. Dependency of $\bar{\nu}_{max}$ of the complex ACE-3,5DNPA on S_M in per- or polyhalogenated (——) and halogenated(---) solvents.

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[*] In the previously reported results[2] carbon tetrachloride and chloroform were exceptions in the relation $\bar{\nu}_{Max}$ vs S_M for the complex acenaphthene-TCPA. The small number of solvents studied in that case did not permit us to interpret this particular behaviour.

[†] In the plot of the absorption maxima of iodine vs I_D (the donor ionization potential) cyclohexane, n-heptane were also correlated with the aromatic solvents.[4]

[‡] For abbreviations see Table 2.

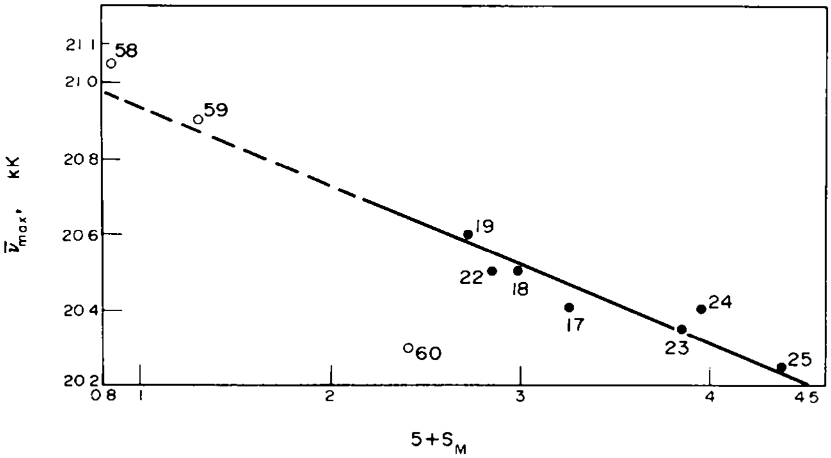

Figure 2. Variation of $\bar{\nu}_{max}$ of the complex ACE-3,5DNPA with S_M in aromatic (●) and miscellaneous (○) solvents.

polar in the ground state. This is contrary to other aromatic-I_2 complexes studied in detail.[22]

It is probable that the general polarity-polarizability parameters (S_M, Z, E_T, ...) are not adequately used in this case. If $\bar{\nu}_{max}$ is plotted against $\Delta\bar{\nu}_D$*, a positive slope (~20) is obtained showing that the n-donor property of the halogenated solvents play the more important rôle. The slope of $\bar{\nu}_{max}$ in eV vs I_D (eV) is ≈0·2, showing again the specific character of the solvation by these solvents. Let us emphasize, that the solvent effect on the absorption of iodine in the same solvents is very similar, where the n-donor character of these solvents are mainly responsible for the shift.[4] While direct relationship $\bar{\nu}_{max}$ vs Z gives a slope near unity for the complexes DMA-TNB (0·84) and DMA-TCNB (0·99),[21] the slope obtained initially with S_M (or E_T) and recalculated vs Z gives 0·2 and 0·3 respectively. Those very large slopes cannot be explained easily for these complexes where the ground state is less polar. The main reason for this discrepancy is the inclusion of "anomalous" Z values (*l*) of cyclohexane, heptane, hexane and 2,2,4-trimethylpentane) in the correlation. Without these solvents, the correlation for the halogen containing solvents alone gives slopes equal to ~0·3 and ~0·2 respectively. Voigt's results[16] present also similar anomalies: while plotted directly vs Z, the slope for the complex oDMOB-TCNE is 0·7, it is only 0·35 with S_M or E_T values. These latter parameters have the advantage to give a greater number of solvents. These remarks show the precaution to take when only one solvent parameter is used with very limited number of solvents.

Since specific effects play a great rôle in the case of complexes where the ground state is less polar than the excited state, well chosen solvents are needed (at least 10 of them) in order to establish a correlation. This must be emphasized, because literature data abound in partial results with partial conclusions which are often erroneous.

Let us note finally that the slopes of $\bar{\nu}_{max}$ vs Z for the $\pi-\pi^*$ and $n-\pi^*$ transitions of $\alpha\beta$ conjugated 9-decalenone are respectively −0·25 and +0·35.[23] The solvent effect on simple molecules or on complexes is rather very similar, as it has been noted by Symons and Davis.[29]

Because the Franck-Condon state is directly reached in the excited state, the magnitude of the solvent effect vs Z does not give the amount of charge-transfer in the excited state as it was proposed for the reaction rates,[24] where the activation complex is supposed to be in thermal equilibrium with environment.

In Fig 3, $\bar{\nu}_{max}$ is plotted against $\Delta\bar{\nu}_D$ for the complex 2,6 DMON-TCPA. The correlation is very good and this holds also for the complexes ACE-3,5DNPA and 9MANT-TCPA. In the case of n-donor solvents, their n-donor ability is the more important factor as it was shown previously;[2] these solvents cause a blue shift proportional to their n-donor ability. A theoretical explanation was already given in Ref 2.

For the complex ANT-3, 5DNPA, the points are rather scattered in the region above $\Delta\bar{\nu}_D = 75$ cm^{-1}. Aromatic solvents with n-donor groups (Table 1: 27, 28, 51 and 56) do not follow the straight line obtained for n-donor solvents. They seem to follow a similar correlation with $\Delta\bar{\nu}_D$ displaced somewhat to lower wave numbers from the "purely" n-donor solvents, because of the polarisable aromatic ring. Let us emphasize that these same solvents do not follow the $\bar{\nu}_{max}$ vs S_M relationship.

For three complexes the sensitivity of $\bar{\nu}_{max}$ to the n-donor parameter is about the same (slope ~5), and for the other two, the sensitivity is about twice as great (slope ~10). The reason for this phenomenon is not clear at present. The slope of aromatic n-donor solvents is similar to that of n-donor solvents, showing that a special property (n-donor ability) is added to the general effect (polarity-polarisability of the aromatic ring). Let us emphasize that literature data also give slopes equal to ~5 or ~10.

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*$\Delta\bar{\nu}_D = \bar{\nu}_S - \bar{\nu}_B$ where $\bar{\nu}_S$ is the stretching vibration frequency (O-D) of deuterated methanol in solvent S and $\bar{\nu}_B$ is the same vibration in the reference solvent benzene. $\Delta\bar{\nu}_D$ is thus the n-donor parameter.[30]

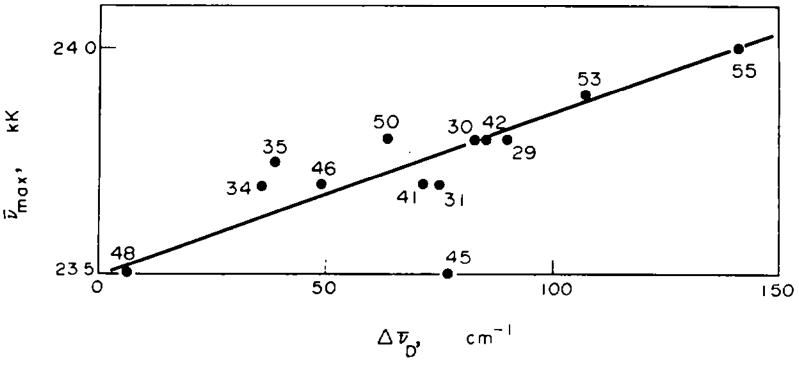

Figure 3. Relation between $\bar{\nu}_{max}$ of the complex 2,6DMON-TCPA and the n-donor solvent parameter $\Delta\bar{\nu}_D$ in n-donor solvents.

Table 2. The values of the slopes $\bar{\nu}_{max}$ (kcal mol^{-1}) vs Z (kcal mol^{-1}) in the case of per- or polyhalogenated (class aI), halogenated (class aII) and aromatic (class b) solvents. The values of the slopes $\bar{\nu}_{max}$ (cm^{-1}) vs $\Delta\bar{\nu}_D$ (cm^{-1}) for the n-donor solvents (class c)

Complex	Slope $\bar{\nu}_{max}/Z$			Slope $\bar{\nu}_{max}/\Delta\bar{\nu}_D$	Ref
	Class (a) I	Class (a) II	Class (b)	Class (c)	
ACE-3, 5DNPA	−0·16	−0·35	−0·2	~10	[a]
ANT-3, 5DNPA	−0·16	−0·45	−0·2	~5(5)[b]	[a]
9-MANT-TCPA	−0·14	−0·35	−0·25	11·5	[a]
2,6-DMON-TCPA	−0·07	−0·45	−0·25	5·1	[a]
ACE-TCPA	—	−0·45	−0·45	4·8	2
p-DMOB[c]-TCNE	−0·3	−0·45	−0·45	—	16
o-DMOB[d]-TCNE	−0·35	—	−0·25	—	16
HMB[e]-TCPA	—	—	−0·55[f]	—	18
HEB[g]-I_2	+0·2	—	—	~20(−0·2)[o]	19, 20
DMA[h]-TNB[i]	−0·2	—	—	—	21, 32
DMA-TCNB[j]	−0·3	—	—	—	21
ACE-CA[k]	−0·2	—	—	—	21
PYR[l]-CA	−0·2	—	—	—	21
HMB-TR[m]	—	—	—	5	27
ANT-TR	—	—	—	~10	27
PYR-TR	—	—	—	~10	27
ANT-A[n]	—	—	—	5, 9	27
LiBr-TCNE	—	—	—	~10	28
HMB-CA	−0·05	—	—	—	29
HMB-NTDA[p]	−0·05	—	—	—	29, 31
ANT-NTDA	—	—	−0·5	—	7
HMB-NTDA	—	—	−0·25	—	7
PER[r]-NTDA	—	—	−0·25	—	7
3,4-BPYR[s]-NTDA	—	—	−0·3	—	7
PYR-NNA[t]	—	—	−0·3	—	7
ANT-NNA	—	—	−0·25	—	7
3,4-BPYR-NNA	—	—	−0·4	—	7

Note: the slopes calculated from literature values are very approximate because of the paucity of data available.

[a] This work; [b] the value in parenthesis is for aromatic n-donor solvents; [c] p-dimethoxybenzene; [d] o-dimethoxybenzene; [e] hexamethylbenzene; [f] in both emission and absorption; [g] hexa-ethylbenzene; [h] N-dimethylaniline; [i] sym trinitrobenzene; [j] 1, 2, 4, 5-tetracyanobenzene; [k] chloranil; [l] pyrene; [m] tropylium tetrafluoroborate; [n] N-methylacridinium perchlorate; [o] slope obtained with $\bar{\nu}_{max}$ (eV) vs I_D, the ionization energies of the solvents(4); [p] 1, 4, 5, 8-naphthalene tetracarboxylic dianhydride; [r] perylene; [s] 3, 4-benzopyrene; [t] 3-nitro-1,8-naphthoic anhydride.

We can conclude from the variation of $\bar{\nu}_{max}$ in different solvents, that the following classification is suggested: class (a) *halogenated solvents*, group I: per- or polyhalogenated solvents; group II. monohalogenated solvents, class (b) *aromatic solvents*, class (b) *n-donor solvents*, group I: "pure" n-donor solvents, group II, aromatic n-donor solvents. This classification seems to be rather general.[2]

We have also examined the variation of the half-band width ($\bar{\nu}_{max} - \bar{\nu}_{1/2}$) of the CT band with the solvent ($\bar{\nu}_{1/2}$ is the wavenumber at the half intensity of the band at its bathochromic side).

The parameter S_M shows a much better correlation, but differ from complex to complex. The aromatic solvents show an increasing tendency of $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ with S_M in the case of the complexes ACE-3,5DNPA and ANT-3, 5DNPA. In the case of ACE-TCPA an opposite behaviour was observed previously.[1] The complex 2,6-DMON-TCPA does not vary with S_M, while the complex 9MANT-TCPA shows a complete dispersion of points.

The halogen-containing solvents do not give any correlation with S_M for 9MANT-TCPA and ANT-3,5DNPA, there is no variation in the case of 2,6DMON-TCPA, while the half-band width increases with S_M for ACE-3,5DNPA. No correlation seems to exist between $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ and $\Delta\bar{\nu}_D$ of n-donor solvents except for the complex 2,6-DMON-TCPA (positive slope). For these solvents the molar volume turns out to be a much better parameter in all cases (negative slope). It seems that the smaller the solvent molecules the better they solvate the complex.[1] This causes a loosening of the complex, hence the greater value of the half-band width.

At present, the behaviour of $\bar{\nu}_{max} - \bar{\nu}_{1/2}$ as a function of various parameters cannot be satisfactorily explained.[1]

EXPERIMENTAL

Materials. Tetrachlorophthalic anhydride (Fluka) was purified by several sublimations, mp 255°C. 3,5-dinitrophthalic anhydride was obtained from the corresponding di-acid by dehydration with acetic anhydride (mp 163·3°C). It is handled under nitrogen. The di-acid (mp 226°C) was synthesized from the 3,5-dinitrotoluic acid by oxidation with nitric acid (d = 1·15) in sealed tubes at 143°C. Acenaphthene (Fluka) was recrystallized five times from aqueous ethanol, mp 95–96°C. Anthracene (U.C.B.) was molten with solid KOH and fractionally crystallized from petroleum ether, mp 216°C. 9-Methylanthracene was recrystallized thrice from methanol, mp 80–81°C. 2,6-Dimethoxynaphthalene (Aldrich) was washed with aqueous sodium hydroxide and recrystallized from aqueous ethanol (mp 152–153°C). The solvents were purified by normal methods and were dried on molecular sieves.

Measurements. The spectrophotometric measurements were carried out with a Unicam SP 800 Spectrophotometer at 20 ± 0·1°C. The wave number scale was standardized against a holmium filter.

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