Charge-transfer Complexes in Organic Chemistry. Part VI.[1] Solvent Effects on Charge-transfer Absorption Bands. Interpretation of the Behaviour of *n*-Donor Solvents †

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The charge-transfer complex formed between acenaphthene and tetrachlorophthalic anhydride has been examined in 32 solvents. In order to explain the general and specific solvent effects, the solvents have been divided into several groups namely protic, dipolar aprotic, aromatic with or without functional groups, and *n*-donor solvents. The results show that if special effects contribute strongly to the solute–solvent interaction, then they will determine the overall solvent effect. An explanation is suggested for the case of *n*-donor solvents. The possibility of predicting polarity changes during excitation is explored.

We have systematically studied solvent effects on the electronic spectra of charge-transfer complexes.‡ There are few studies of this problem and the most extensive ones are devoted essentially to general solvent effects.[2] The results can be roughly categorised as follows. When solvent polarity increases (*a*) a blue shift of the charge-transfer (CT) band is observed if the ground state is ionic and the excited state is not ionic,[2–6] (*b*) a red shift is observed when the ground state is not ionic and the excited state is ionic (the solvent effect is less pronounced is this case [7–15]), and (*c*) blue or red shifts are observed in the cases where both the ground state and the excited state are ionic.[3,16,17]

This oversimplified classification cannot properly explain solvent effects since it is based only on overall effects and ignores specific ones.[18]

The first systematic study [11] on non-ionic ground-state complexes distinguished essentially two types of solvents, protic (alcohols) and aprotic (chlorine-containing). Surprisingly Foster and Emslie found a blue shift for the first type of solvent while the second type caused the expected red shift with increasing solvent polarity. The authors explain this difference by the formation of a 'rigid cage' around the complexes in the protic solvents. Both for protic and aprotic solvents the spectral shifts could be well correlated with *Z*-values.[19] However, the *n*-donor solvents did not follow the correlation. The same anomalies were reported by other workers.[3,6,20,21]

Several authors have tried to explain the anomalous blue shift caused by the increasing solvent polarity for neutral ground-state complexes. Czekalla and Meyer [8] call upon the change of enthalpy, while Davis and Symons [22] suggest an explanation in terms of a new charge distribution in the ground state. A similar suggestion [9] (see also ref. 23) is that in polar solvents, the mixing of no-bond and dative structures is enhanced, bringing about a larger splitting of the energy levels, hence the blue shift.

We interpret our results in terms of different empirical solvent parameters. S_M Values are used for general effects stemming from polarity and polarisability [S_M is the logarithm of the second-order rate constant k_M of the quaternisation of tri(n-propyl)amine by methyl iodide [24]] while $\Delta\bar{\nu}_D$ values are applied to account for specific effects due to the electron-donating power (*n*- or π-type) of the solvent ($\Delta\bar{\nu}_D$ is the variation of the O–D stretching frequency of monodeuteriated methanol in various solvents with benzene chosen as standard [25]).§

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‡ By charge-transfer complex we mean any molecular association having a new absorption band in the u.v. or visible spectrum.

§ The parameter $h\nu_{CT}$ was suggested [1] to represent special effects caused by the π-donor ability of the solvents only ($h\nu_{CT}$ is the charge-transfer transition energy of the complexes formed by aromatic compounds and iodine [13]).

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RESULTS AND DISCUSSION

The charge-transfer absorption maxima, $\bar{\nu}_{max.}$, of the complex acenaphthene (ACE)–tetrachlorophthalic anhydride (TCPA) were examined in 32 different solvents belonging to the following classes (*a*) halogen-containing, (*b*) aromatic, (*c*) aromatic with one functional group, and (*d*) *n*-donor solvents (Table 1). These solvents were chosen to represent not only general [(*a*) and (*b*)] but also specific (*d*) and mixed (*c*) effects and to cover the whole range of the general effect.

TABLE 1

Solvent effect on the charge-transfer absorption band of the acenaphthene–tetrachlorophthalic anhydride complex ACE–TCPA at 20 °C

Solvent	$\bar{\nu}_{max.}$/kK	ε_0 *	$\frac{n^2-1}{2n^2+1}$ †	$\Delta\bar{\nu}_D$/cm^{-1}	$3 + S_M$
Class (*a*)					
Carbon tetrachloride (CCl_4)	24·6	2·236	0·217	−21	0·146
n-Butylchloride (Bu^nCl)	24·9	7·3	0·1958		1·114
Dichloromethane (DCM)	24·3	9·08	0·2035	−12	2·447
Chloroform (Clf)	24·1	4·80	0·2104	−17	2·114
1,2-Dichloroethane (DCE)	24·3	10·65	0·2104	2	2·580
1,1,2,2-Tetrachloroethane (TCE)	24·15	8·50	0·229		2·940
1-Chlorohexane (ClH)	24·95	5·90	0·2019		0·892
Class (*b*)					
Benzene (B)	24·5	2·283	0·2277	0	1·255
m-Xylene (*m*X)	24·7	2·374	0·2264		0·716
p-Xylene (*p*X)	24·8	2·27	0·2260		0·740
Toluene (T)	24·65	2·39	0·226	2	0·978
Class (*c*)					
Chlorobenzene (ClB)	24·25	5·70	0·2346	−2	1·845
Bromobenzene (BrB)	24·15	5·46	0·2444	−1	1·949
Benzonitrile (BN)	24·5	25·65	0·235	38	2·591
Benzaldehyde (BA)	24·55	17·85	0·2406	53	2·556
Pyridine (Py)	24·2	13·3	0·2536	168	2·431
Class (*d*)					
n-Butyraldehyde (BUA)	25·15	13·4 §	0·1896	83	
Tetrahydrofuran (THF)	25·2	7·61	0·1965	90	1·462
Tetrahydropyran (THP)	25·3			93	
Acetonitrile (AN)	25·0	36·8	0·1753	49	2·670
Nitromethane (NM)	24·8	37·45	0·1928	6	3·040
Nitroethane (NE)	24·9	29·11	0·1922	8	2·663
Dimethylformamide (DMF)	25·3	38·42	0·2043	107	2·778
Dimethyl sulphoxide (DMSO)	25·45	49·0	0·22	141	3·2
Ethyl acetate (EA)	25·0	6·20	0·1848	39	1·343
Diethyl ether (DE)	25·1	4·35	0·178	78	0·079
Acetone (A)	25·15	21·07	0·180	64	2·176
Dimethylacetamide (DMAC)	25·35	37·78		113	(2·6) ‡
1,4-Dioxan (DX)	24·65	2·22	0·2037	77	1·568
1,2-Dimethoxyethane (DMOE)	25·0	(3·5—6·8)	0·1905		(1·5) ‡
Miscellaneous					
Cyclohexane (CH)	25·05	2·02	0·204		2·845
Carbon disulphide (CS_2)	24·1	2·64	0·2613		0·398

* Ref. 24 and ' Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 1964. † Ref. 2 and HCP. ‡ Estimated values from the E_T/S_M [28,29] correlation. § At 26 °C.

No correlation can be obtained between $\bar{\nu}_{max.}$ and the dielectric constant ε_0 which represents the solvent polarity.* Polarisability $[(n^2 - 1)/(2n^2 + 1)]$ gives a better general trend but cannot be simply correlated with $\bar{\nu}_{max.}$.

The difference between these two results is reasonable if we bear in mind that ε_0 is closely related to molecular movements of orientation in the solvation shell, while polarisability concerns only an electronic rearrangement.

We might therefore expect that a parameter containing both polarity and polarisability terms would give a better relationship. Choosing S_M as such a parameter (on account of the large number of values now available) we can see that this is indeed the case (Figure 1).

The correlation between $\bar{\nu}_{max.}$ and S_M for the chlorine-containing (*a*) (except for CCl_4 and Clf) and the aromatic (*b*) solvents gives two separate straight lines. An increase in solvent polarity and polarisability (S_M increases) causes, as expected (*vide supra*) a red shift of

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* An increasing red shift in the order THF, A, and AN with ε_0 was also observed for the *n*–π complex formed between piperidine and αα′-dicyano-4,4′-dinitrostilbene.[26] The total absence of a correlation between $\bar{\nu}_{max.}$ and ε_0 shows that this parallelism is fortuitous because only a very limited number of solvents were investigated.

[26] O. B. Nagy and A. Bruylants, *Bull. Classe Sci. Acad. Roy. belges*, 1967, [5], **53**, 934, 947, 1159.

the absorption band. The aromatic solvents with one functional group (*c*) split into two groups. The first (ClB and BrB) falls on the line for the aromatic solvents.

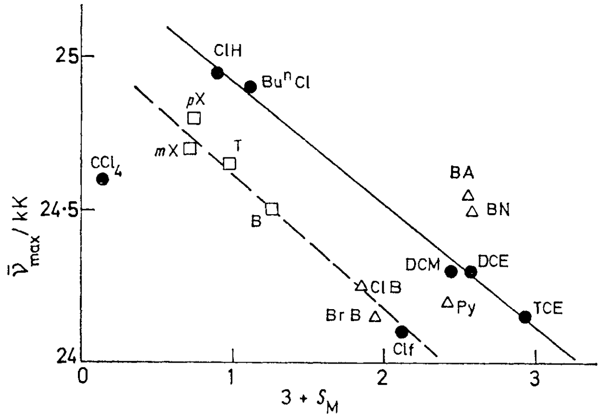

FIGURE 1 Correlation of $\bar{\nu}_{max.}$ with the S_M values in the case of aromatic (☐), halogen-containing (●) and aromatic solvents with one functional group (△)

The second (BA, BN, and Py), having both π-donor (aromatic ring) and *n*-donor (functional group) properties, is not correlated.

The *n*-donor solvents (*d*) show a scatter of points. This is in complete agreement with all the results reported where these solvents are considered as ' exceptions.' [3,6,11,20] However, if we use the *n*-donor property ($\Delta\bar{\nu}_D$) as solvent parameter, excellent correlation is obtained (Figure 2). Except for dioxan (DX) the points are on a straight line. *n*-Donor solvents cause a blue shift proportional to their *n*-donor ability. This result suggests that *n*-donor solvents are not at all ' exceptions ' but should be considered as a separate class of solvents acting mainly by a specific effect.

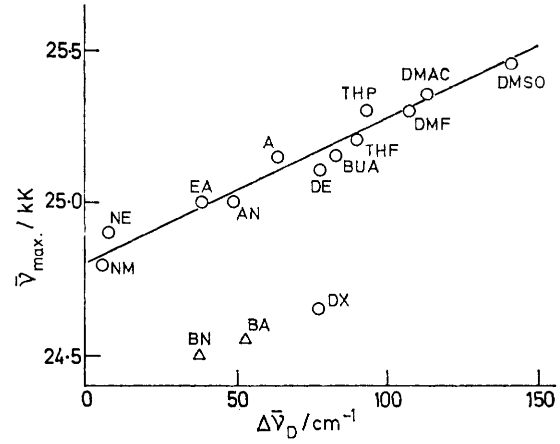

FIGURE 2 Correlation of absorption maxima with the *n*-donor parameter, $\Delta\bar{\nu}_D$

We suggest the following explanation for their behaviour. In the solvation shell the solvent dipoles try to align themselves with the dipole of the solute molecules. On the other hand their mutual repulsions will tend to force them to a perpendicular position with respect to the solute. The solvent dipoles tend to occupy the energetically most favourable orientation which will thus be neither parallel nor perpendicular. Therefore this can be characterised by a mean angle $\bar{\beta}$ formed by the dipoles of the solvent and the dipole of the solute molecules.*

For non-ionic states the solvation is less and the value of the equilibrium $\bar{\beta}$ is closer to 90° than for ionic states. Therefore the variation of the energy of a non-ionic ground state (G.S.) and a more polar or ionic excited state (E.S.) with the mean angle $\bar{\beta}$ can be represented by † Figure 3.

The specific solvation of the solute by the free electron pairs of the *n*-donor solvent molecules makes the latter adopt a perpendicular position to the solute dipole so that the accessibility of the free electron pair is increased. This shifts the minimum of the ground-state energy curve toward 90°. However the energy curve of the excited state is almost unaffected by this special effect because it is mainly influenced by general effects (polarity and polarisability). This is due to its more polar character. Therefore, following the Franck–Condon principle, we should observe a blue shift when passing from a weak *n*-donor ($h\nu_1$) to a strong *n*-donor ($h\nu_2$) ‡ solvent. This must be true for any complexes that exhibit increasing polarity when passing from the ground to the excited state.

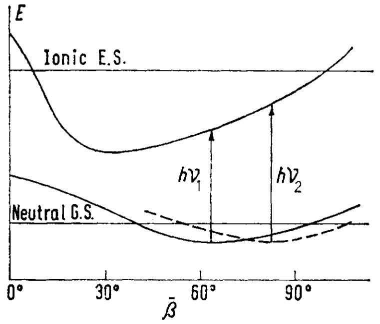

FIGURE 3 *n*-Donor solvent effect on the CT transition energy

This explanation seems reasonable and it is supported strongly by the fact that solvents reported as exceptions [9,11] also follow the predicted $\bar{\nu}_{max.}/\Delta\bar{\nu}_D$ relationship. However, a few exceptions exist such as 1,4-dioxan (DX), maybe due to its high flexibility, and benzonitrile (BN) and benzaldehyde (BA) because of the presence of aromatic rings.

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* The dipole of the solute molecules is the actual overall dipole resulting from charge-transfer as well as from local dipoles of the donor and acceptor moieties.

† Similar considerations were used [27] to explain the Stokes shift in the fluorescence spectra.

‡ This is provided that the orientation of the overall dipole does not change too much during the excitation.

[27] E. Lippert, ' Optische Anregung organischer Systeme,' Verlag Chemie, Weinheim, 1966, p. 342.

Complexes with ionic or more polar ground states and non-ionic excited states (Class **1**, see below) could not be correlated with $\Delta\bar{\nu}_D$ showing that in this case the general effects prevail (*e.g.* *Z*-values do not correlate with $\Delta\bar{\nu}_D$).[2-6, 19, 28, 29]

Particularly interesting are the complexes formed between ions and neutral molecules (Class **3**).[2, 3, 16, 17] In this case both the ground state and the excited state are ionic. The correlation $\bar{\nu}_{max.}/\Delta\bar{\nu}_D$ gives a positive slope ($\bar{\nu}_{max.}$ increases with $\Delta\bar{\nu}_D$). In the light of our results we can conclude that the ground state is less polar than the excited state. The preceding analysis shows that whenever special solvent effects intervene strongly in the solute–solvent interaction, they determine essentially the overall solvent effect. By using two different solvent parameters expressing either general (*Z*, E_T, and S_M values) or specific (*e.g.* $\Delta\bar{\nu}_D$ values) effects one can easily determine the relative polarity of the ground and excited states of charge-transfer complexes. The effects are summarised in Table 2.

TABLE 2

Possible solvent effect correlations of $\bar{\nu}_{max.}$

	Polarity		Correlation	
Class	G.S.	E.S.	General effects (*Z*)	Specific effects ($\Delta\bar{\nu}_D$)
1	Polar or ionic	Neutral	Yes; positive slope	No
2	Neutral	Polar or ionic	Yes; negative slope	Yes; positive slope
3	Polar or ionic	More polar or ionic	Yes or no	Yes; positive slope

This Table is only tentative. It is limited only to a few examples reported in the literature and its validity needs to be tested for a large number of solvents. To do so one has to keep in mind that all the solvents cannot be compared directly but rather have to be divided into several classes such as protic, dipolar aprotic, aromatic with or without functional groups, halogen-containing, *n*-donor solvents, *etc.* Only within one single class can correlations be sought. Even in this case exceptions will exist for several reasons. These can be the particular structure (of CT complexes or of solvents), the individual solvation of the complex forming partners, *etc.*

Our conclusions are contrary to the explanation[9] of the observed ' anomalous ' blue shift. We do not ignore the existence of increased splitting in polar solvents but we think that it is overshadowed by general and specific solvent effects which have been completely neglected[9] (Figure 4). Furthermore the arguments have been based on a very limited number of solvents. Still, the ' normal ' red shift with increasing polarity was observed except for the *n*-donor solvents. For these *n*-donor solvents, the specific effect should be important, as we have shown, causing the expected blue shift. In the case of the strong pyridine–iodine complex a normal red shift was observed with increasing solvent polarity.[30]

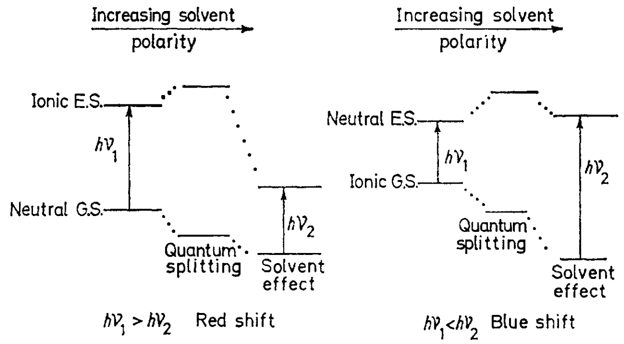

FIGURE 4 Quantum and solvent effects on charge-transfer transition energy; G.S. = ground state; E.S. = excited state

For a few strong complexes (*n*–σ or *n*–π types) a blue shift was reported in accord with Abidi and Offen's hypothesis[9] even in the case of non *n*-donor solvents.[23, 31-33] We suggest that the ground state of these complexes is more ionic than the excited state and not less ionic as it was supposed.[23] However in these cases the increased splitting could successfully compete with the solvent effect. More experimental and theoretical studies are needed to settle this problem.

EXPERIMENTAL

Materials.—Tetrachlorophthalic anhydride (TCPA) (Fluka) was purified by several sublimations, m.p. 254·5—255·5 °C. Acenaphthene (Fluka) was recrystallised five times from aqueous ethanol, m.p. 95—96 °C. The solvents were purified by normal methods and were dried finally on molecular sieves.

Measurements.—The spectrophotometric measurements were carried out with a Unicam SP 800 spectrophotometer at 20 °C. The wave number scale was standardised against a holmium filter.

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