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The Electronic Spectra of Intramolecular Charge-transfer Compounds and Their Marked Solvatochromism in a Strong Hydrogen-bonding Solvent: 2-(Arylmethylene)-1,3-indandiones and 2-(1-Naphthyl)-*p*-benzoquinone

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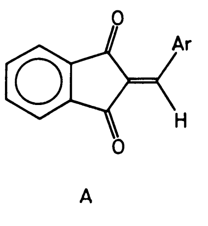
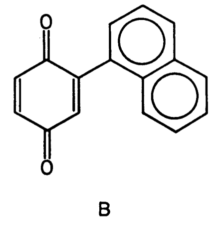
The first electronic absorption bands of the title compounds can all be assigned to the intramolecular charge-transfer transitions. The solvent effects on these bands are quite analogous to those on the absorption bands characteristic of binary charge-transfer complexes. Especially, when the title compounds are dissolved in trifluoroacetic acid, marked bathochromic shifts of the first bands are observed, in harmony with their charge-transfer character. Such solvatochromism is obviously due to the hydrogen-bond formation between the solute and the solvent molecules. When strong hydrogen bonding occurs, the electron affinity of the 2-methylene-1,3-indandione moiety increases by about 0.41 eV.

Very many papers have so far been published concerning binary charge-transfer (CT) complexes in the solution phase.[1] The physical and chemical properties of these complexes have thus been clarified widely. However, our understanding of intramolecular CT compounds in solution is still far from satisfactory.[2–4] Here, an intramolecular CT compound is an organic compound in which an electron-attracting group with a large electron affinity is attached to an electron-donor molecule, forming a single conjugated system as one whole.[3] This kind of compound has the following two characteristics. First, as in the case of binary CT complexes, the first electronic absorption bands are mostly related to the charge-transfer, each within a single conjugated system. Second, such compounds are structurally much less flexible in solution than binary CT complexes. This might make the analysis of the electronic spectra much less ambiguous than that of binary CT complexes. It is noteworthy that some aspects of the solution spectra of binary CT complexes remain elusive.[5] This is primarily due to the fact that the general response of a CT transition to a solvent is inconsistent with the dielectric theory of solute-solvent interactions.[6] In this context, we can fully expect that some intramolecular CT compounds might be useful in exploring further the intrinsic features of CT-type transitions.

In this paper, we would like to present the first systematic survey of the electronic transitions typical of the intramolecular CT compounds. The first absorption bands of 2-(arylmethylene)-1,3-indandiones (**A**) and 2-(1-naphthyl)-*p*-benzoquinone (**B**) will be examined below in conjunction with the solvent effects on binary CT complexes.



A



B

Experimental

The 2-(arylmethylene)-1,3-indandiones listed in Table 1 and 2-(1-naphthyl)-*p*-benzoquinone were prepared and purified according to the procedures found in the literature.[7,8] In each of them, a ring system with two carbonyl groups bonds a benzenoid compound. The absorption spectra of these compounds were measured using a Beckman DK-2A spectrophotometer. All the solvents were of a guaranteed grade and were used without further purification.

Intramolecular CT Character of the First Absorption Bands

An intramolecular CT transition is defined as an electronic transition from an occupied molecular orbital localized in a part of a conjugated system to an unoccupied molecular orbital localized in the other part of the same conjugated system.[2–4] All the 2-(arylmethylene)-1,3-indandiones (**A1**—**7**) and 2-(1-naphthyl)-*p*-benzoquinone (**B**) exhibit intramolecular CT bands isolated on the low-energy side of the electronic absorption spectra. The intramolecular CT character of the first absorption bands was verified as follows.

First, the molecular orbital (MO) calculations provide theoretical evidence for it. The Pariser-Parr-Pople MO calculations carried out by Meyer[9] and by us[10] indicate that, for all compounds investigated, the highest occupied molecular orbital (HOMO) is localized mainly at the benzenoid ring, whereas the lowest unoccupied molecular orbital (LUMO) is localized mainly at the 2-methylene-1,3-indandione (or *p*-benzoquinone) ring. Accordingly, the benzenoid ring can be considered as a good electron donor, as usual, and the methyleneindandione (or *p*-benzoquinone) ring as a good electron acceptor. Meyer has already assigned the first absorption band of 2-benzylidene-1,3-indandione to the lowest intramolecular CT transition.[9] The situation is exactly the same for the other compounds.

The MO calculations show that a geometrical HOMO-LUMO separation depends straightforwardly upon the dihedral angle between a benzenoid donor ring and an acceptor ring.[10] For most of the compounds

TABLE 1. INTRAMOLECULAR CT ABSORPTION BANDS OF 2-(ARYLMETHYLENE)-1,3-INDANDIONES IN CHLOROFORM

Aryl group (Ar)	$\frac{h\nu_{ICT}}{10^3\ cm^{-1}}$	$\varepsilon^{a)}$	$I_p{}^{b)}$/eV
Phenyl (**A1**)	29.09	33400	9.24$^{c)}$
Styryl (**A2**)	25.95	45100	8.60$^{d)}$
1-Naphthyl (**A3**)	24.81	17600	8.12$^{c)}$
2-Naphthyl (**A4**)	27.35	29100	8.12$^{c)}$
p-Dimethylaminophenyl (**A5**)	20.78	86400	7.51$^{e)}$
1-Pyrenyl (**A6**)	20.51	43700	7.41$^{f)}$
9-Anthryl (**A7**)	20.25	10700	7.40$^{c)}$

a) Extinction coefficient. b) Vertical ionization potential. c) Ref. 12. d) R. A. W. Johnstone and F. A. Mellon, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1155 (1973). e) Ref. 13. f) Ref. 14.

in Table 1, it is not possible to take a planar configuration because of serious steric hindrance. This structural feature is quite favorable to the HOMO-LUMO separation, thus improving the intramolecular CT character of the first absorption band. Especially, a large dihedral angle between the two parts of 2-(9-anthrylmethylene)-1,3-indandione (**A7**) can be inferred from the small extinction coefficient of the first absorption band.

In a simplified MO treatment,[11)] the overlap integral between two bonded $2p_z$ orbitals which belong to different chromophores is found to be proportional to cos Θ, where Θ is the dihedral angle between them, and the absorption intensity may be expected to be proportional to $\cos^2\Theta$. The extinction coefficient of the first band of **A7** is about one-eighth that of 2-(*p*-dimethylaminobenzylidene)-1,3-indandione (**A5**) and about one-fourth that of 2-(1-pyrenylmethylene)-1,3-indandione (**A6**). We may assume that the donor ability is almost the same for these three compounds, since the ionization potentials of the isolated donors (*i.e.*, anthracene, *N*,*N*-dimethylaniline, and pyrene) are nearly equal to each other.[12–14)] Therefore, if we assume **A5** and/or **A6** to be planar in shape, the dihedral angle in **A7** must be at least 60°. This angle can be justified by inspecting a molecular model of this compound.

Next, the good acceptor ability of a methyleneindandione ring is supported by the crystal structure of **A5**.[15)] The methyleneindandione ring of each molecule is therein in close contact with the *p*-dimethylaminophenyl ring of its adjacent molecule, the two forming a CT-type self-complex. Since the donor part has a good electron-donating character, such a self-complex formation in the solid phase witnesses the good acceptor ability of the methyleneindandione ring.[2,4,16)] The electron affinity of *p*-benzoquinone is 1.89 eV;[17)] it is also a good electron acceptor, even if it becomes a part of a larger conjugated system, as in the case of 2-(1-naphthyl)-*p*-benzoquinone. The intramolecular CT character of the first absorption bands of several 2-aryl-*p*-benzoquinones has previously been confirmed experimentally.[4,16)]

Finally, the most conclusive proof of the intramolecular CT character is obtained by plotting the electronic absorption maximum against the ionization potential of the donor part for **A1**—**7**. In general, a CT transition energy is linearly related to an ionization potential of the donor molecule if the acceptor molecule is common to all the CT complexes concerned.[18,19)] In the case of intramolecular CT compounds with common acceptor parts, an intramolecular CT transition energy, $h\nu_{ICT}$, may analogously be expressed as:

$$h\nu_{ICT} = a_1 I_p - b_1, \qquad (1)$$

where a_1 and b_1 are constants characteristic of the acceptor part and where I_P is, of course, an ionization potential of the donor part, *e.g.*, an ionization potential of anthracene in the case of **A7**.

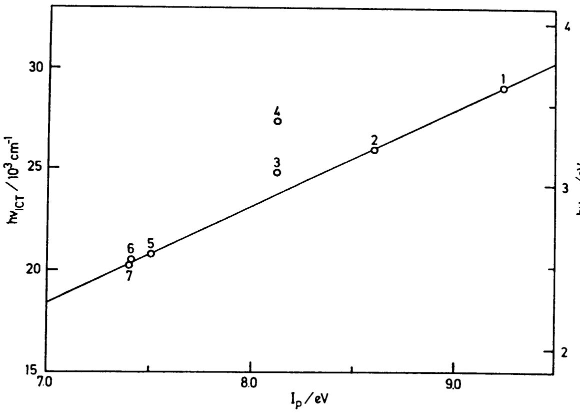


Fig. 1. Correlation of the intramolecular CT absorption maxima with the donor ionization potentials: 1, **A1**; 2, **A2**; 3, **A3**; 4, **A4**; 5, **A5**; 6, **A6**; **7**, **A7**.

As is shown in Fig. 1, this relationship was found to hold well for most 2-(arylmethylene)-1,3-indandiones dissolved in chloroform. The two exceptions are the 1- and 2-naphthylmethylene derivatives (**A3** and **A4**). For the other compounds, $a_1=0.592$ and $b_1=1.840$ when $h\nu_{ICT}$ and I_P are given in units of eV. Although the absorption maxima of the two exceptional compounds deviate upward from Eq. 1, there are clear absorption shoulders near the energy predicted by this relationship. They are located at 23500 cm^{-1} for **A3** and at 25000 cm^{-1} for **A4**. There may be some structural factor in these intramolecular CT compounds which causes a marked change in the Franck-Condon envelope. The appearance of such a vibrational structure is not unusual when an intramolecular CT compound is dissolved in a relatively inert solvent.[4)] Accordingly, we can safely say that Eq. 1 is valid for all 2-(arylmethylene)-1,3-indandiones. It is, then, quite natural to attribute the first absorption band of every compound in Table 1 to an intramolecular CT transition between HOMO and LUMO. For binary CT complexes in solution, the a_1 value lie in the 0.83—0.97 range,[1)] a little larger than that for the intramolecular CT bands considered above. According to Flurry's MO description of CT transitions,[19)] the $a_1=0.592$ value indicates that 1.592 of the two frontier electrons reside in the donor ring in the ground state. Consequently, these intramolecular CT compounds can really be regarded as undissociable CT complexes.

Solvatochromism Caused by a Strong Hydrogen-Bonding Solvent

If a given electronic absorption band is of the CT type, its solvent dependence might be similar to that of binary CT complexes.[5] In order to examine this possibility, the first absorption maxima of **A7** in various solvents were plotted against the dielectric constants of the solvents[20] (*cf.* Fig. 2). In general, *n*-donor solvents, such as ketones, alcohols, and nitriles, shifted the intramolecular CT band to the higher-energy side. This spectral aspect is quite consistent with that of binary CT complexes,[1] but is evidently contrary to the prediction of the dielectric theory of solute-solvent interactions.[6] Such a response to solvents further supports the CT character of the electronic transition concerned.

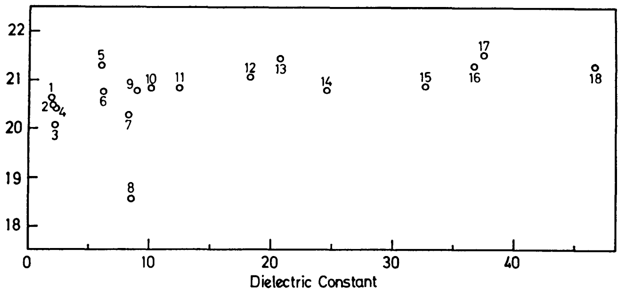


Fig. 2. The first absorption maximum of **A7** as a function of solvent dieletric constant: 1, hexane; 2, cyclohexane; 3, carbon tetrachloride; 4, benzene; 5, ethyl acetate; 6, acetic acid; 7, 1,2,2,2-tetrachloroethane; 8, trifluoroacetic acid; 9, dichloromethane; 10, 1,2-dichloroethane; 11, pyridine; 12, cyclohexanone;13, acetone; 14, ethanol; 15, methanol; 16, *N*,*N*-dimethylformamide; 17, acetonitrile; 18 dimethyl sulfoxide.

When the intramolecular CT compounds were dissolved in trifluoroacetic acid (TFAA), an unusually large bathochromic shift of the first absorption band occurred. In 1975, Sep *et al.* observed very large bathochromic shifts of the CT bands when anthracene complexes with typical acceptors were dissolved in TFAA.[21] The same effect can be seen in Fig. 2, where TFAA (8) marks a singular point, as in the case of binary CT complexes.[21] In order to analyze such bathochromism induced by TFAA, we used dichloromethane (DCM) as the reference solvent. The dielectric properties of these two solvents are quite similar to each other.[20] The dielectric constants are 8.55 for TFAA and 8.93 for DCM. The refractive indexes are 1.285 for TFAA and 1.421 for DCM. This pair of solvents, therefore, lend themselves to the study of specific solvation effects.

It is noteworthy that, for the compounds investigated, the energy difference between the first absorption bands of the DCM and the TFAA solution amounts to 1270—2400 cm^{-1}. By the way, the second absorption band of **A7** is a local-excitation band, in the sense that the molecule is excited locally at the anthracene ring.[10] The 0-0 vibrational component of this band is located at 26400 cm^{-1}, while that of the first band of anthracene is located at 26400 cm^{-1}, too, both in DCM. The vibrational spacing of the former band is about 1380 cm^{-1}, which is comparable to that of the latter band (1415 cm^{-1}). In contrast to the first band of **A7**, the TFAA-to-DCM shift of the second band (*i.e.*, the local-excitation band) is about 200 cm^{-1}, about one-tenth that of the first intramolecular CT band. The TFAA-to-DCM solvent shift of the intramolecular CT band is thus an order of magnitude larger than that of an allowed excitation band localized in a nonpolar conjugated hydrocarbon ring.

Such an anomalous bathochromic shift of the intramolecular CT band begins to occur when only a drop of TFAA is added to a few ml of the DCM solution. When the amount of TFAA reaches a certain mol %, the TFAA effect on the absorption spectrum becomes substantially saturated. After that, the absorption peak remains almost unmoved. In other words, the curve of a peak position versus the solvent composition is linear, with essentially no slope, as long as the concen-

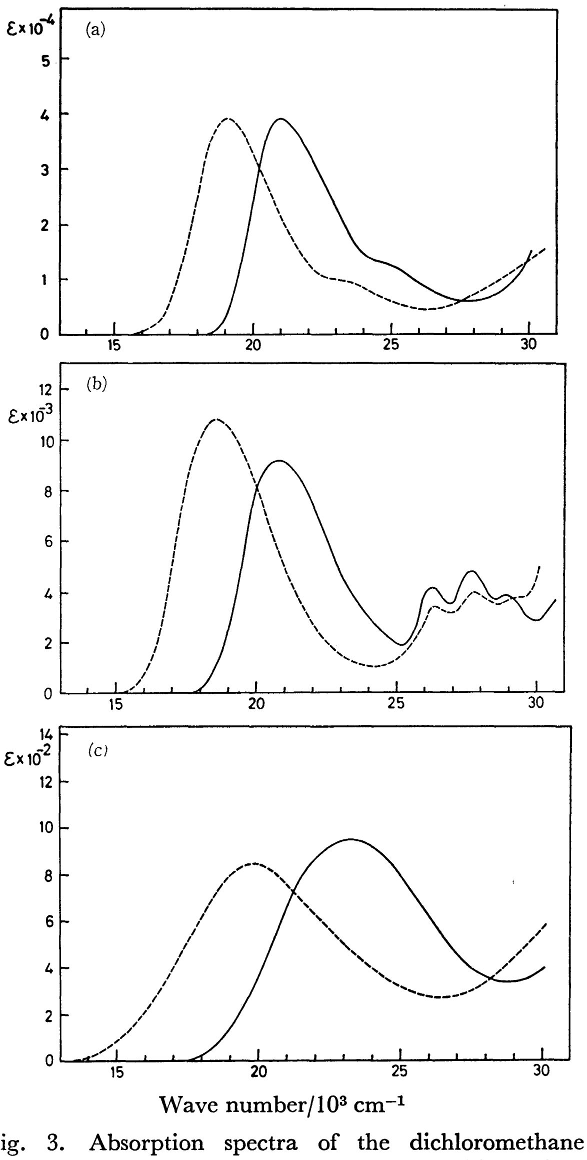


Fig. 3. Absorption spectra of the dichloromethane solutions (——) and the trifluoroacetic acid solutions (----): (a), **A6**; (b), **A7**; (c), **B**.

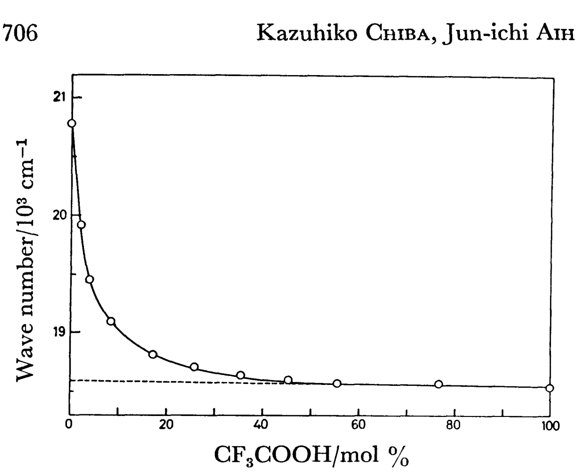


Fig. 4. The intramolecular CT absorption maximum as a function of solvent composition of the CH$_2$Cl$_2$–CF$_3$COOH–**A7** system.

tration of TFAA is sufficiently high. Figures 3 and 4 illustrate this situation. Let the linear portion in the curve be extrapolated to the 100% pure DCM solution, and we can, in principle, estimate the peak position of the TFAA solution which would be exhibited if TFAA had exactly the same dielectric properties as DCM. The slope of this linear portion, if any, might be interpreted as due to a slight difference in dielectric properties between TFAA and DCM.

Accordingly, an extrapolated point in the energy scale, $h\nu_0$, can be taken as the reference energy in evaluating the degree of specific solvatochromism caused by TFAA. A net bathochromic shift not due to the dielectric properties of TFAA can, then, be expressed as:

$$\Delta h\nu_{\mathrm{ICT}} = h\nu_{\mathrm{ICT}} - h\nu_0. \qquad (2)$$

Here, $h\nu_{\mathrm{ICT}}$ indicates the energy of the first absorption maximum of the TFAA solution. The numerical values concerning Eq. 2 are all listed in Table 2. As for this expression, one exceptional compound may be 2-(1-naphthyl)-*p*-benzoquinone, for which there is little linear portion in the band-peak *versus* solvent-composition curve. In this case, the tangent at the 100% pure TFAA solution was extrapolated to the other end of the solvent composition. Fortunately, the tangent had no inclination.

TABLE 2. BATHOCHROMIC SHIFTS OF INTRAMOLECULAR CT BANDS OF 2-(ARYLMETHYLENE)-1,3-INDANDIONES AND 2-(1-NAPHTHYL)-*p*-BENZOQUINONE IN TRIFLUOROACETIC ACID

Compd[a]	$h\nu_{\mathrm{ICT}}$/10^3 cm^{-1}		$\Delta h\nu_{\mathrm{ICT}}$	ΔE_{a}
	CH$_2$Cl$_2$	CF$_3$COOH[b]	10^3 cm^{-1}	eV
A1	29.15	27.88(27.88)	1.27	0.27
A2	26.02	24.13(24.13)	1.89	0.40
A3	25.00	22.60(22.60)	2.40	0.50
A4	27.83	25.88(25.88)	1.95	0.41
A6	20.92	19.01(19.01)	1.91	0.40
A7	20.78	18.54(18.59)	2.19	0.46
B	23.22	19.80(19.80)	3.42	—

a) See Table 1 for abbreviations. b) Values for $h\nu_0$ are given in parentheses.

As may be seen from Table 2, $\Delta h\nu_{\mathrm{ICT}}$ is almost the same as the energy difference between the first absorption bands of the DCM and the TFAA solution. The value of $\Delta h\nu_{\mathrm{ICT}}$ stays in the 1270—2400 cm^{-1} range for 2-(arylmethylene)-1,3-indandiones and is somewhat larger for 2-(1-naphthyl)-*p*-benzoquinone.

It has been established that a protic solvent often shifts the CT absorption band to the blue side.⁵⁾ However, the direction of the TFAA solvent shift, defined by Eq. 2, is obviously the opposite of that expected on going from DCM to a protic solvent. The primary effect of TFAA on the intramolecular CT bands is totally different from that of familiar protic solvents. On the other hand, the strong hydrogen-bonding ability of TFAA has been proved by C-13 NMR investigations of various ketones.²²⁾ The chemical shifts show that TFAA molecules attach selectively to carbonyl oxygens in a hydrogen-bonding manner. Sep *et al.* also observed such an effect on acid anhydrides by means of C-13 NMR spectrometry.²¹⁾ In this sense, TFAA is in marked contrast to ethanol, which may act as a proton acceptor rather than as a proton donor.²³⁾ The same situation must be true in the present case. The $\Delta h\nu_{\mathrm{ICT}}$ quantity can, hence, be interpreted as due to hydrogen bonding between the solute and the solvent molecules.

Here, we should note that, when hydrogen bonding effectively occurs between solvent molecules and a molecule of the type shown in Table 1, the acceptor ability related to the LUMO of the solute is improved because of the increased core charge on each carbonyl oxygen.²¹⁾ The donor ability related to the HOMO can, nevertheless, be expected to remain almost unchanged because of the geometrical HOMO-LUMO separation. Therefore, the energy shift of the intramolecular CT band in TFAA can be ascribed mostly to a change in the electron affinity of the acceptor part.

By analogy with Eq. 1, the following expression may hold for intramolecular CT compounds with common donor parts:

$$h\nu_{\mathrm{ICT}} = -a_2E_{\mathrm{a}} + b_2, \qquad (3)$$

where E_{a} is the electron affinity of the acceptor part and where a_2 and b_2 are constants characteristic of the common donor part. In the CT-excited state, the charge on the donor part decreases to the same extent as the charge on the acceptor part increases. As both a_1 in Eq. 1 and a_2 in Eq. 3 are determined principally by the degree of charge transfer,¹⁸˒¹⁹⁾ we can assume that a_2 is close to a_1 for the same group of intramolecular CT compounds. Thus, the change in the acceptor electron affinity on going from DMC to TFAA can be evaluated as:

$$\Delta E_{\mathrm{a}} = -\Delta h\nu_{\mathrm{ICT}}/a_1. \qquad (4)$$

By the use of experimental values for $\Delta h\nu_{\mathrm{ICT}}$, an increase in the electron affinity of the methyleneindandione part, on the average, is calculated to be 0.41 eV in TFAA. A larger amount of change in electron affinity is conceivable for 2-(1-naphthyl)-*p*-benzoquinone in TFAA.

It has been inferred from analogous bathochromic shifts of the intermolecular CT bands that the electron affinities of typical acceptor molecules in association with anthracene might also be enhanced in the same solvent.[21] However, in the case of binary CT complexes, the position and the orientation of an acceptor, relative to those of a donor, are not firmly fixed in the solution phase because the binding energy between the two components is very small.[1] Both components must be fluctuating rather independently as a result of thermal agitation. Strong hydrogen bonding may further deform the shape of the complex when it is dissolved in TFAA. For binary CT complexes, a linear portion in the band-peak versus solvent-composition curve has an appreciable slope, although the same pair of solvents (*i.e.*, TFAA and DCM) are employed[21]. This may reflect the nonrigidity of binary CT complexes in solution. On the other hand, the present results on intramolecular CT compounds are mostly free from ambiguities arising from these factors. The distance between the donor and the acceptor is kept unchanged because of the existence of a direct bond between them. Therefore, we might safely say that the shift of an intramolecular CT absorption band is indeed due to the increased electron affinity of the acceptor part, but a similar conclusion with regard to binary CT complexes[21] appears a bit less decisive.

Remarks

In addition to 2-(arylmethylene)-1,3-indandiones and 2-(1-naphtyl)-*p*-benzoquinone, we have examined the solvatochromism of many other compounds of the intramolecular CT type. However, when one or more hetero atoms were present in the π-electron framework of the donor part, it was not easy to analyze the resulting solvation effect in detail. For example, solvent effects on **A5** are not simple because specific interactions occur between solvent molecules and hetero atoms in both the donor and acceptor parts. When more than a small amount of the solvent effect on the acceptor side is cancelled by that on the donor side, it is quite difficult to separate the overall solvent shift between the two sides of the molecule. The absorption spectrum of **A5** in TFAA is totally different from that in DCM. For this reason, the present study had to be limited strictly to intramolecular CT compounds in which there are no hetero atoms in the donor part. The donor parts of these compounds are supposedly inert to the hydrogen-bonding effect of TFAA. Such compounds, each with a single kind of substituent on the acceptor side, were, hence, most suitable for analyzing a specific solvation effect induced by TFAA.

According to the simple CT theory,[1] a vibrational structure of a CT absorption band might be characteristic of the acceptor component because a CT transition may naively be viewed as an electron jump to the LUMO localized in the acceptor.[24] In the present case, the band shape scarcely changes even when a strong hydrogen bonding occurs between solute and solvent molecules. This may imply that the vibrational modes which determine the contour of the intramolecular CT absorption band are little affected by the hydrogen-bond formation. In line with this, there is no drastic change in the absorption intensity, either.

In this context, Kuboyama *et al.* assigned the first absorption band of 4-pyrone to the intramolecular CT transition from the ethereal oxygen to the carbonyl group.[25] The solvent shift induced on going from heptane to 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) is quite large (*ca.* 1200 cm^{-1}). HFP is also a strong hydrogen-bonding solvent.[21] However, the shape of the intramolecular CT band is somewhat deformed in this solvent. This is probably due to a considerable reorganization of the π-electron framework of 4-pyrone, since its whole conjugated system is very compact. The existence of a second, but very weak, absorption band was predicted near the intramolecular CT band;[25] it may also be responsible for the deformation of the CT band.

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