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Intramolecular Donor−Acceptor Interactions in Jet-Cooled Bichromophoric Molecules: Comparison between $SiMe_2$ and CMe_2 Spacers

A. Zehnacker* and F. Lahmani*

Laboratoire de Photophysique Moléculaire du CNRS, Bât. 213, Université de Paris,
XI 91405 Orsay Cédex, France

C. A. van Walree and L. W. Jenneskens

Debye Institute, Department of Physical Organic Chemistry, Utrecht University,
Padualaan 8, 8584 Utrecht, The Netherlands

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The laser-induced excitation and dispersed fluorescence spectra of a series of bichromophores consisting of para-substituted benzene moieties linked by a CMe_2 or a $SiMe_2$ spacer have been investigated under solvent-free conditions in a supersonic expansion. The spectroscopic properties of three different systems involving the benzonitrile−benzonitrile, the anisole−benzonitrile, and the *N*,*N*-dimethylaniline−benzonitrile pairs have been examined and compared to the monomeric units. For the isolated bichromophores, the lowest fluorescent excited state is localized on the aromatic moiety with the lowest excited state and does not reveal strong perturbation due to the presence of the second aromatic subunit. In the anisole−benzonitrile system where the localized excitations are expected to be close in energy, the lowest excited state is localized on the anisole moiety for the CMe_2 spacer and on the benzonitrile moiety in the case of the $SiMe_2$ spacer. In this latter example, a second intense transition has been assigned to the excitation of the anisole chromophore. The emission following excitation of this upper level is characteristic of the benzonitrile chromophore, indicating that irreversible electronic energy transfer takes place in this system. In the dimethylaniline−benzonitrile bichromophores, the excitation and dispersed emission show that the lowest excited state is localized on the dimethylaniline subunit and that no electron-transfer process takes place under isolated conditions. Complexation of carbon- and silicon-bridged donor−acceptor compounds with acetonitrile results in the appearance of an intense continuous absorption extending over a large energy range and a Stokes shifted emission that can be assigned to a charge-transfer state.

Introduction

Nonconjugated bichromophores consisting of a donor and an acceptor moiety covalently linked by an aliphatic spacer have been widely used as model systems to study the interaction between neighboring aromatic rings at the molecular level. The wide choice of chromophores provides a way of understanding the coupling between locally excited states that is responsible for the exciton splitting for symmetric systems and electronic energy transfer (EET)[1] for disymmetric ones, or the coupling between a locally excited state and an ionic state, resulting in a charge-transfer (CT)[2,3] process. The electronic coupling between the two chromophores depends on the properties of the spacer such as its size, conformation, flexibility, and electronic structure, which determine the relative distance and mutual orientation of the interacting species and are responsible for so-called through-space- and through-bond-mediated interactions.

The spectroscopy and dynamics of bichromophoric molecules under jet-cooled conditions are expected to shed light on the mechanism of electronic energy transfer and charge transfer in the absence of solute−solvent interactions. Under these conditions, the effect of the solvent that stabilizes the electronic states and induces vibrational relaxation is eliminated. On the other hand, the species in solution can show a large distribution of different isomers, whereas only the most stable conformation(s) are trapped at the low temperature achieved under jet-cooled conditions.

The study of electronic energy transfer and electron transfer in isolated bichromophores has shown that these processes can be described within the frame of the radiationless transitions theory. Electronic energy transfer under jet-cooled conditions has been investigated by Levy et al.[4,6,7] and Speiser et al.[5] and described in a review by the latter author.[1] The factors that influence the efficiency of EET, as determined by the Fermi Golden Rule, have been investigated. Among them, the energy gap between the donor and the acceptor is of first importance because it determines the density of vibrational states in the final state. The geometry of the bichromophore that determines the relative orientation of the donor and the acceptor and the distance between them has also been shown to play a crucial role: Upon it depends the interaction between the transition moments, for a Förster-type mechanism, or the overlap between the excited-state orbitals, for a Dexter-type mechanism. An example of particular relevance is the case of perpendicular bichromophoric spiranes[6,7] in which the electronic energy transfer is forbidden by symmetry at the zero level but was shown to proceed very efficiently through vibronic coupling involving nonsymmetric deformations of the molecule.

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* Corresponding authors. E-mail: anne.zehnacker@ppm.u-psud.fr.

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Photoinduced intramolecular charge transfer has also been the subject of numerous studies under solvent-free conditions,[2] since the pioneering work of Zewail's group.[8,9] Two limiting mechanisms have been proposed for this process:

For donor−acceptor pairs linked by a flexible bridge, there is a low-energy barrier for the charge-transfer process that occurs at short distance, in a folded conformation of the molecule. This folded geometry, which brings the donor and the acceptor in close contact, results from intramolecular vibrational redistribution (IVR). In this case, the low-frequency modes of the chain play an important role in facilitating the IVR process.[2] The same mechanism has been invoked for intermolecular electron transfer in donor−acceptor van der Waals complexes.[10]

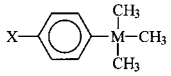
For donor−acceptor pairs bridged by a semirigid spacer, a harpooning mechanism occurring at large distance in an extended configuration of the bichromophore has been proposed.[2,11] In this case, the barrier for charge transfer (and thus the appearance of a CT-type Stokes shifted emission) has been shown to be lower than the conformational barrier needed to bring the donor and acceptor in close contact. This observation led Jortner et al. to propose a sequential two-step mechanism: [12,13] the charge separation occurs in the first step and results in a charge-transfer state in the extended geometry, whereas in the second step, the Coulombic attraction induces the folding of the bichromophore and leads to the emissive exciplex state observed in jet-cooled experiments. The nature of the spacer is important in this regard, as it can modify the distance between the donor and the acceptor and thus the Coulombic attraction term.

We have recently studied the influence of the nature of a three-atom chain on the efficiency of excimer formation in symmetric bichromophores[14,15] or exciplex formation in bichromophores made up of naphthalene and anthracene linked by a methylene or ether chain.[16] In these systems, the coupling between the chromophores is quite weak due to the large distance between them. We present here a comparative spectroscopic study of monatomically bridged diphenyl derivatives (CMe_2 or $SiMe_2$ bridge) under jet-cooled conditions as an extension of the recent work of van Walree et al. in solution and in the solid state.[17] The aim of this work is 2-fold: first, it appears interesting to investigate systems in which the aromatic moieties are held in close proximity, due to the small size of the monatomic bridge. Second, very little has been reported until now about intramolecular charge transfer in jet-cooled silicon-containing molecules.[18] A comparative study of the properties induced by the CMe_2 or $SiMe_2$ spacers is thus interesting in this regard. Van Walree et al. have already compared the solution properties of the compounds containing *N*,*N*-dimethylaniline (DMA) as the donor and benzonitrile as the acceptor. The study of the solvent dependence of the radiative lifetime and the maximum of the CT emission led to the conclusion that the electronic coupling between the locally excited (LE) state and the charge-transfer (CT) state is larger for the carbon-containing species, although its charge-transfer state lies at higher energy than that of the silicon-containing one. The larger coupling term has been explained by the shorter distance between the donor and the acceptor in the carbon-containing species.

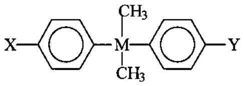
To get a better understanding of the electronic coupling at play in these bichromophores, the photophysical properties of the jet-cooled C- and Si-bridged compounds have been compared for three systems: the symmetric bisbenzonitrile compounds, the anisole−benzonitrile bichromophores, and the strong donor−acceptor pairs consisting of *N*,*N*-dimethylaniline and benzonitrile. For the sake of comparison, the subunits have also been studied as model systems. The molecules under study are listed in Chart 1.

CHART 1

Model compound	M	X
DMA-C	C	Me₂N
DMA-Si	Si	Me₂N
CN-C	C	CN
CN-Si	Si	CN



Bichromophore	M	X	Y
DMA-C-CN	C	Me₂N	CN
DMA-Si-CN	Si	Me₂N	CN
MeO-C-CN	C	MeO	CN
MeO-Si-CN	Si	MeO	CN
CN -C-CN	C	CN	CN
CN -Si-CN	Si	CN	CN



Besides a comparison between $SiMe_2$ and CMe_2 spacers, we also present results on complexation with a polar solvent (acetonitrile). The role of "microsolvatation" (complexation) by a polar solvent in inducing intramolecular charge transfer has been extensively studied in DMABN derivatives[19,20] or conjugated systems such as bianthryl[21] for which solvation has been shown to be necessary to induce the charge-transfer process.

Experimental Section

The experimental setup for jet experiments is the same as that previously used.[14] Briefly, it consists of a continuous supersonic expansion of helium (2−3 atm backing pressure) expanded through a 200 μm pinhole. The bichromophores are slightly heated just before the expansion to obtain enough vapor pressure and are excited by a frequency-doubled dye laser (Rh6G or C540A) pumped by the second or the third harmonic of a YAG laser (Quantel). Fluorescence was observed either through a filter (WG 310 for the resonance fluorescence, WG 385 for the charge-transfer state fluorescence) or dispersed through a 60 cm Jobin-Yvon monochromator. The lifetimes were measured by a 9400 Lecroy oscilloscope working in the sweeping mode. The temporal resolution of the laser is 8 ns.

The synthesis of the compounds under study has been described elsewhere.[17]

Results

The compounds under study are presented in Chart 1, and the S_0−S_1 transition energies are collected in Table 1.

I. Spectroscopy of Symmetric Systems: CN-Containing Compounds. The fluorescence excitation spectra of the bichromophores CN−C−CN and CN−Si−CN are presented in Figure 1a,c. For the sake of comparison, the excitation spectra of the monomers CN−C and CN−Si are also shown in Figure 1b,d. The 0−0 transitions of CN−C−CN and CN−Si−CN are located at 36 079 and 35 665 cm^{-1}, respectively, and exhibit redshifts of 266 and 132 cm^{-1}, respectively, relative to those

TABLE 1: S_0−S_1 0−0 Transition Energies and Fluorescence Decay Times under Supersonic Jet Conditions of Monosubstituted Aromatic Reference Compounds and the Bichromophores under Study

chromophore	0−0 transition (cm^{-1})	lifetime ($\upsilon = 0$) (ns)
tert-butyl benzene	37 696[a]	[b]
phenyltrimethylsilane	37 730[c]	[b]
anisole	36 386[d]	23
DMA	32 896[e]	[f]
DMA−C	32 571	[f]
DMA−Si	32 876	[f]
benzonitrile	36 512[g]	70
CN−C	36 345	32
CN−Si	35 797	34
CN−C−CN	36 079	31
CN−Si−CN	35 665	31
MeO−C−CN	35 493	[b]
MeO−Si−CN	35 712	32
DMA−C−CN	32 225	[f]
DMA−Si−CN	32 600	[f]

[a] From Hopkins et al.[23] [b] Not Measured. [c] From Teh et al.[30] [d] From Lahmani et al.[24] [e] From Weersink et al.[26] [f] Within the laser pulse. [g] From Kobayashi et al.[22]

of the monomers CN−C and CN−Si (Table 1). It should be noted that the 0−0 transitions of silicon-containing compounds are shifted to the red by more than 400 cm^{-1} relative to the carbon-containing ones for both the dimers and the monomers. The fluorescence lifetimes of both bichromophores are very close to those of the monomers (see Table 1).

Several differences between the spectral characteristics of the excitation spectrum of CN−C−CN and CN−Si−CN are observed:

We can compare the relative intensity of the 0−0 band, which is only due to the Franck−Condon component of the transition moment, to that of the ν_{6b} band around 500 cm^{-1}, which is known to borrow intensity via Herzberg−Teller coupling from the L_a state. The 0−0 band of the silicon-containing species is four times as intense as the ν_{6b} band whereas the 0−0 band and the ν_{6b} band are of the same intensity in the carbon-containing species. This shows that the S_0−S_1 electronic transition is more allowed in the silicon-containing molecule than in the carbon analogue where the vibronic coupling between the L_a and the L_b states is responsible for an important part of the transition intensity. This statement has been confirmed by the molar extinction coefficients in solution.

The most remarkable difference between CN−C−CN and CN−Si−CN is the presence in the latter molecule of a bunch of bands that follow the origin transition. Although very weak bands at 28 cm^{-1} and 92 cm^{-1} appear in CN−C−CN and no low-frequency pattern appears in the model systems, CN−Si−CN displays in the 0−0 transition region four features separated by a 13 cm^{-1} interval. They display a peculiar intensity distribution that exhibits an odd/even alternance. The dispersed fluorescence spectra obtained by pumping the 0−0 transition and the most intense band at 25 cm^{-1} are identical and lack the corresponding low-frequency vibration in the ground state (vide infra). Such a structure in the 0−0 transition region is not observed in the case of CN−C−CN. The dispersed emission obtained by pumping the 0−0 transition of CN−C−CN resembles that of the model CN−C (Figure 2a,b). The vibronic bands in the S_0 state at 530 and 638 cm^{-1} have their counterparts in the S_1 state at 494 and 568 cm^{-1} and can be assigned to the 6b and 6a fundamentals, respectively, of substituted benzene (Platt's notation). Dispersed fluorescence obtained by pumping the 0−0 transition of CN−Si−CN also displays a vibronic pattern similar to that of the model compound CN−Si (Figure 2c,d) with the 6b mode located at 536 cm^{-1}. The 1100 cm^{-1} frequency has been assigned to the 7a ring deformation by analogy with benzonitrile.[22] It should to be noted that the progression on the 7a mode at 1100 cm^{-1} provides a clear signature of the CN−Si chromophore.

II. Spectroscopy of the Nonsymmetrical Donor−Acceptor Systems. The bichromophores investigated in this part consist of a benzonitrile unit linked to two donors of increasing strength.

1. Anisole Donor: MeO−C−CN and MeO−Si−CN. The excitation spectra of MeO−C−CN and MeO−Si−CN are shown in Figures 3a and 4a. Although the excitation spectra observed for both bichromophores are located in the same energy range, their spectral characteristics diverge strongly.

a. MeO−C−CN. The excitation spectrum of MeO−C−CN exhibits at the origin two strong bands separated by 130 cm^{-1}. The lowest energy band appears at 35 493 cm^{-1}, and the strongest band is located at 35 623 cm^{-1}. They are shifted to the red of the origin of the monomer CN−C by 852 and 722 cm^{-1}, respectively. The model compound MeO−C was not available for this study, and we shall compare MeO−C−CN and *p*-methylanisole: the bands observed in MeO−C−CN are very close to the origin of S_0−S_1 in *p*-methylanisole[23] (35 400 cm^{-1}). These bands correspond either to two different ground-state isomers or two different excited states localized on each separate chromophore. However, the energy of the S_0−S_1 transition of the monomer CN−C lies about 800 cm^{-1} above the observed 0−0 transition, and the energy gap between the two localized excitations is expected to be larger than the observed difference of 130 cm^{-1}. Moreover, the oscillator strength of benzonitrile is much lower than that of anisole. It thus seems likely that these bands correspond to two ground-state isomers. The dispersed fluorescence obtained by pumping the two main transitions of MeO−C−CN (see Figure 3b,c) confirms this assignment. Both emission spectra behave like a 0−0 transition; their vibrational structures look very similar and are typical of the anisole moiety.[24] Their most intense vibrational band, appearing at 800 cm^{-1}, can be assigned to the substituent-sensitive skeletal deformation mode of the aromatic ring ν_{12} by analogy with anisole. Finally, the dispersed fluorescence of MeO−C−CN strongly differs from that of the monomer CN−C or the symmetrical compound CN−C−CN that exhibit a completely different pattern characteristic of the benzonitrile chromophore. Two conformational isomers corresponding to different orientations of the OCH_3 substituent with respect to a nonsymmetric para substituent have been evidenced in the case of *p*-dimethoxybenzene[25] and *p*-cyclohexylanisole[4] and may also coexist in MeO−C−CN.

b. MeO−Si−CN. The 0−0 band of the bichromophore MeO−Si−CN is located at 35 700 cm^{-1} (97 cm^{-1} to the red of that of the monomer CN−Si). It is followed by a second intense band located at 314 cm^{-1}. The 0−0 band displays a six-membered low-frequency progression built on a 12.5 cm^{-1} mode with a Franck−Condon distribution peaking on the third feature. This shape indicates that the excited-state geometry is modified relative to the ground state along a large-amplitude motion that may be attributed to a torsion of the aromatic rings. This structure is blurred for the 314 cm^{-1} band although the same global envelope is maintained.

The fluorescence decays measured after excitation of different vibronic bands of the 0−0 transition and the 314 cm^{-1} band are almost the same as those of the benzonitrile monomer and range between 32 and 27 ns. This result indicates that the

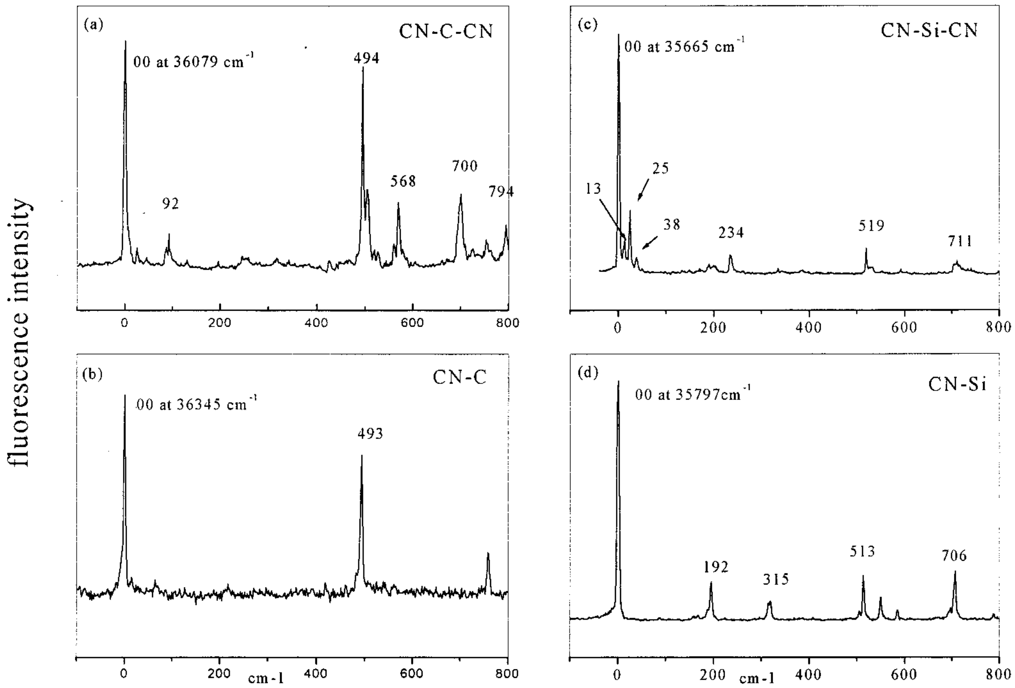


Figure 1. Fluorescence excitation spectra of the symmetric bisbenzonitrile and the related monomers: (a) CN−C−CN, (b) CN−C, (c) CN−Si−CN, and (d) CN−Si.

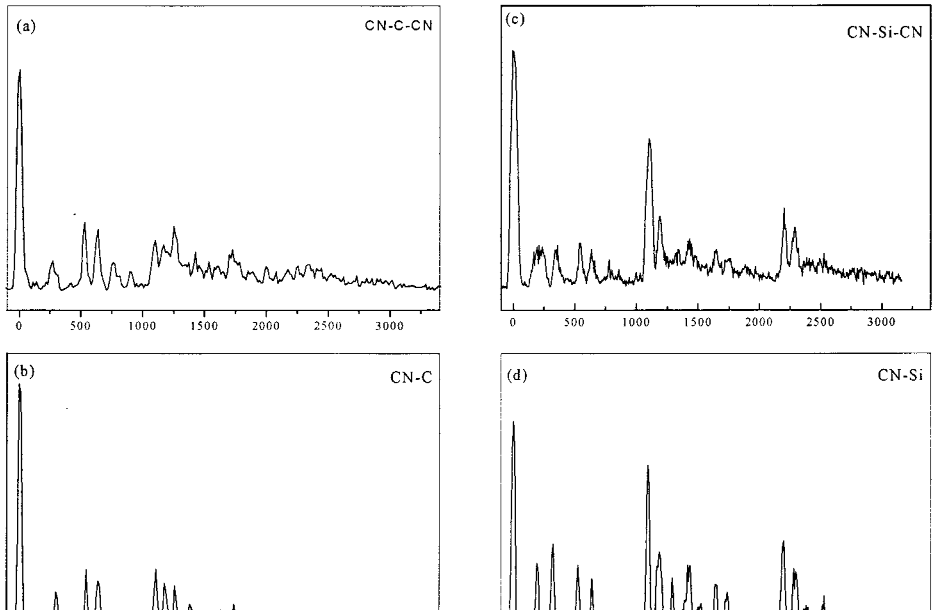


Figure 2. Dispersed fluorescence of the symmetric bisbenzonitrile and the related monomers excited on the S_0−S_1 0−0 transitions: (a) CN−C−CN, (b) CN−C, (c) CN−Si−CN, and (d) CN−Si.

emitting species probably corresponds to the excited state localized on the benzonitrile moiety. The dispersed fluorescence resulting from the excitation of the 0−0 band of MeO−Si−CN displays the same vibrational structure and shows the same characteristic progression on the 1100 cm^{-1} mode as that of the CN−Si monomer or the symmetrical bichromophores built from benzonitrile (Figure 4b,c). This result confirms the nature of the lowest emitting state and shows that, in contrast to the compound MeO−C−CN, the lowest S_0−S_1 transition is localized on the benzonitrile moiety in MeO−Si−CN.

The intensity of the 314 cm^{-1} feature is slightly higher than that of the 0−0 transition and remarkably enhanced in comparison to other vibronic features of much lower intensity at 200 and 500 cm^{-1}. The attribution of this intense band to a vibronic transition of the first locally excited state is thus questionable: a weak feature at 315 cm^{-1} is present in the LIF spectrum of the monomer CN−Si, but the high intensity of the 314 cm^{-1} band precludes its attribution to the same vibrational mode. The most plausible explanation is that it corresponds to the selective excitation of the anisole chromophore, which has a larger transition moment than that of benzonitrile (by a factor of 1.8 when substituted by the trimethylsilyl group) and is thus expected to give rise to a strong 0−0 transition in the excitation spectrum.

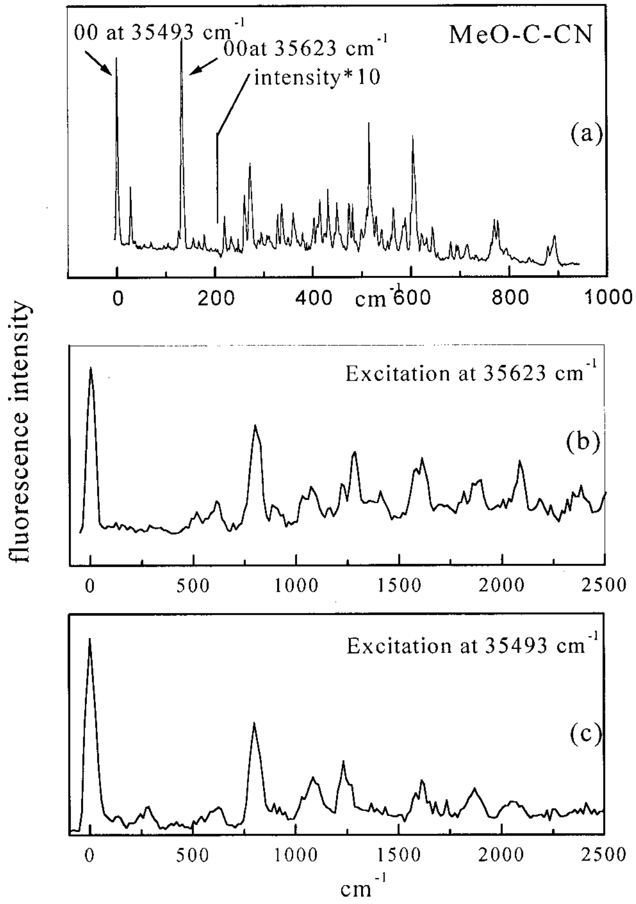


Figure 3. Fluorescence excitation (a) and dispersed emission spectra of MeO−C−CN (b) excited at 35 623 and (c) 35 493 cm^{-1}.

The emission obtained by pumping the band at 314 cm^{-1} exhibits the same progression built on the 1100 cm^{-1} mode, starting from the $\Delta v = 0$ band located at 330 cm^{-1} to the red of the excitation wavelength. It is thus characteristic of the benzonitrile chromophore. This behavior shows that the optically excited anisole moiety evolves toward the lowest electronic excited state localized on the benzonitrile moiety as a result of a fast electronic energy transfer.

2. Dimethylaniline Donor: DMA−C−CN and DMA−Si−CN. Figure 5 shows the fluorescence excitation spectra of the bichromophore DMA−C−CN and DMA−Si−CN together with that of the monomers DMA−C and DMA−Si. It should be noted that the excitation spectrum of DMA−Si−CN is located more to the blue than that of DMA−C−CN (it starts at 32 600 cm^{-1}, whereas the first strong band of DMA−C−CN is at 32 225 cm^{-1}). A similar blueshift is observed for the S_0−S_1 transition of DMA−Si relative to DMA−C.

The spectra of the carbon-containing molecules DMA−C−CN (Figure 5a) and DMA−C (Figure 5b) look very similar and exhibit a complicated vibrational structure close to the origin, which becomes more and more congested when increasing the excess energy. Such a low-frequency structure with a peculiar Franck−Condon distribution has also been observed in dimethylaniline[26,27] and has been assigned the coupled torsion of the methyl groups of the amino substituent. The dispersed fluorescence (see Figure 8) obtained by exciting DMA−C−CN in the 0−0 band is similar to that of the monomer and peaks at about 2000 cm^{-1} from the excitation.

On the contrary, the excitation spectrum of the silicon-containing bichromophore DMA−Si−CN (Figure 5c) differs from that of the monomer DMA−Si (Figure 5d): while the excitation spectrum of the monomer DMA−Si is still structured in the region of the origin located at 32 876 cm^{-1} as in the case of DMA−C, a broadened excitation band peaking at 32 750 cm^{-1} is observed in the case of DMA−Si−CN. A superimposed vibrational structure is however still apparent. It should be noted that the Franck−Condon envelope of the excitation spectrum of DMA−Si−CN is similar to that of MeO−Si−CN but is twice as broad. The dispersed fluorescence of DMA−Si−CN excited at the maximum of its absorption band (shown in Figure 8) is resonant and characteristic of the DMA moiety and does not exhibit the large Stokes shift of the emission that is expected for a CT-type emission.

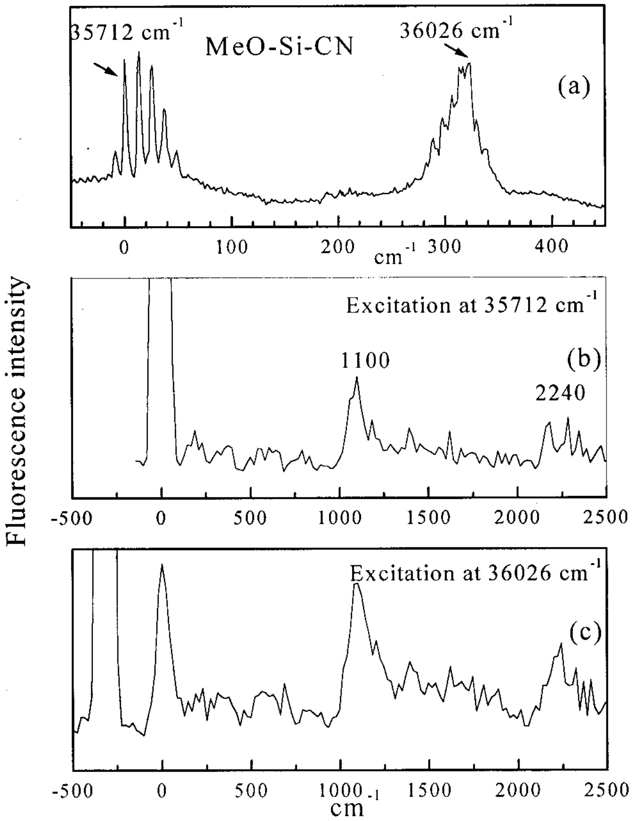


Figure 4. Fluorescence excitation (a) and dispersed emission spectra of MeO−Si−CN (b) excited at 35 712 and (c) 36 026 cm^{-1}.

III. Effect of Complexation of Donor−Acceptor Bichromophores with Acetonitrile. *1. Photoinduced Charge Transfer in MeO−Si−CN.* Complexation of MeO−Si−CN with acetonitrile (1:1 complex) results in a 234 cm^{-1} redshift of the electronic transition, together with an increase of the frequency of the low-vibration mode (24 cm^{-1}). No redshifted emission is observed because the structure appearing in the excitation spectrum disappears when the signal is monitored at $\lambda > 385$ nm: no charge-transfer process takes place in the 1:1 complex (Figure 6).

The broad band that is superimposed on the spectrum of the complex increases when the partial vapor pressure of CH_3CN is increased and thus arises from clusters of larger size. Its lifetime is shorter than that of the bare molecule or the 1:1 complex (20 ns). In contrast, the emission of the larger clusters is much more redshifted because the broad continuum is still present in the excitation spectrum when the fluorescence is monitored at $\lambda > 385$ nm.

2. Photoinduced Charge Transfer in DMA−C−CN. The excitation spectrum of DMA−C−CN in the presence of CH_3CN shown in Figure 7a does not display the structure characteristic of the dimethylaniline chromophore but is broad and

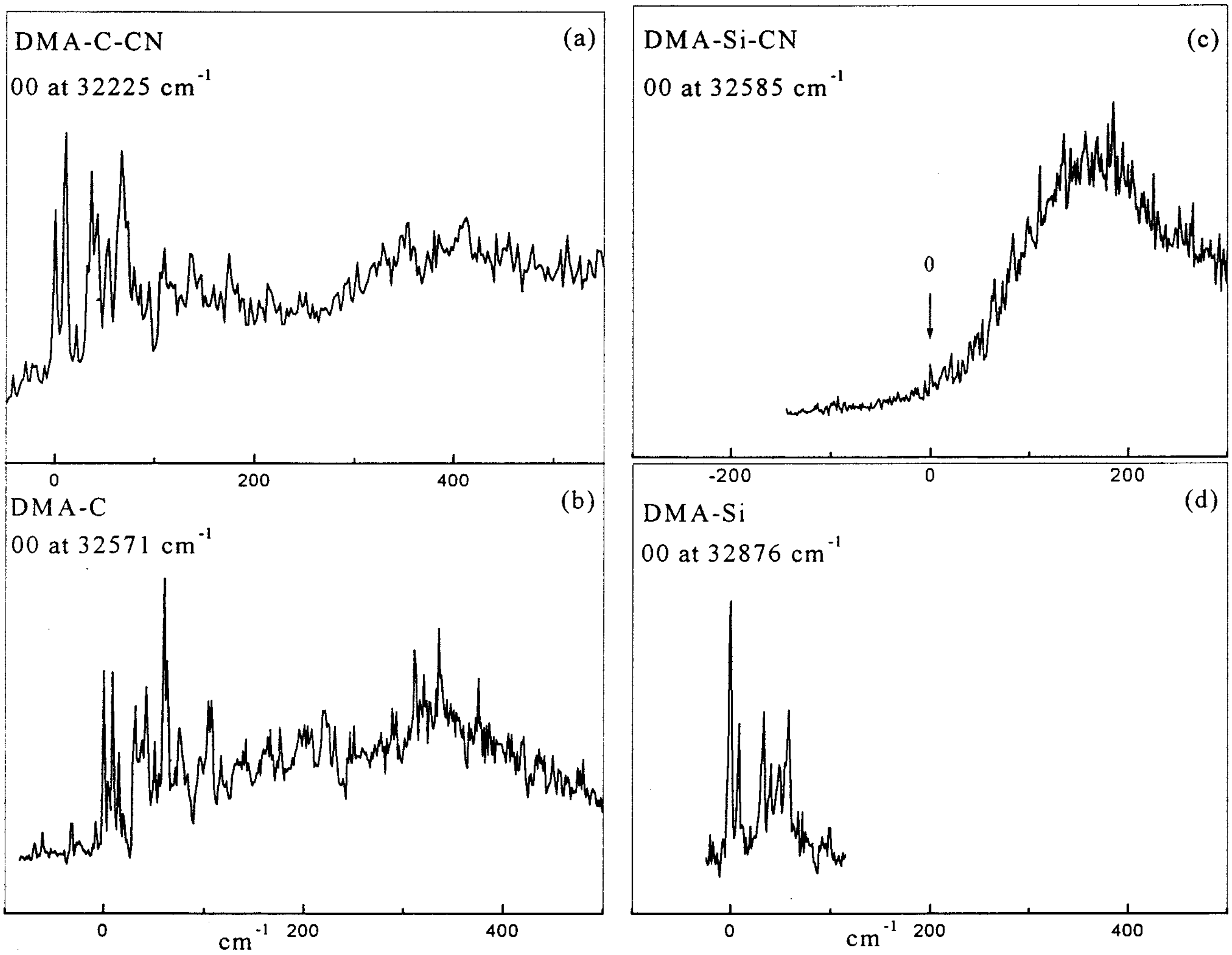


Figure 5. Fluorescence excitation spectra of donor−acceptor bichromophores and related donor components: (a) DMA−C−CN, (b) DMA−C, (c) DMA−Si−CN, and (d) DMA−Si.

continuous over a large energy range extending toward the red of the 0−0 transition of the bare molecule. The intensity of this spectrum depends linearly on the partial pressure of acetonitrile, indicating that the fluorescence results from a 1:1 complex. The low-resolution dispersed emission shown in Figure 8a differs also from that of the bare molecule because it extends by more than 8000 cm^{-1} to the low-energy side, whereas most of the emission intensity of the bare molecule was within 4000 cm^{-1} of the origin. Its maximum is located at 350 nm and corresponds to a Stokes shift of about 3500 cm^{-1}. These results demonstrate that complexation with polar acetonitrile induces the relaxation to a charge-transfer state responsible for the redshifted emission.

3. Photoinduced Charge Transfer in DMA−Si−CN. Figure 7b shows the excitation spectrum of DMA−Si−CN in the presence of CH_3CN. The excitation spectrum of the complex is diffuse and broader than that of DMA−C−CN and extends over more than 1000 cm^{-1} (the apparent decrease in the fluorescence intensity in the red part of the spectrum simply reflects the decrease in the laser intensity). The intensity dependence of the fluorescence upon CH_3CN partial pressure indicates that the fluorescence is due to a 1:1 complex. The emission of the complex (Figure 8b) extends much more to the red than that of the bare molecule and does not show emission within 3000 cm^{-1} from the excitation, in contrast with the behavior of the bare molecule and the complexes of DMA−C−CN with CH_3CN. Its intensity maximum is centered at 370 nm, corresponding to a Stokes shift of 5500 cm^{-1}. This fluorescence can safely be assigned to a charge-transfer type emission.

Discussion

In this section, we will compare the effect of substitution by TMS (trimethylsilyl) or *tert*-butyl on the energy-level position in the model compounds and in the bichromophores. Then, we will examine how the bridge affects the electronic coupling between the subunits for the carbon- and silicon-containing species. Finally, we will discuss the effect of complexation by CH_3CN in relation with what has been observed in solution.

I. Energy-Level Position and Spectral Characteristics. *1. Model Compounds.* As pointed out by van Walree et al.,[17] the effect of para substitution by TMS or *tert*-butyl on the L_b transition of benzene derivatives is different depending whether the first substituent is an electron-accepting or -donating group. For an electron-acceptor (benzonitrile), the L_b transition is shifted to the red by substitution with TMS and *tert*-butyl, but the effect is much larger for TMS (715 cm^{-1}) than that for *tert*-butyl (167 cm^{-1}). This effect has been clearly evidenced in solution and was explained by the electron-attracting properties of the TMS

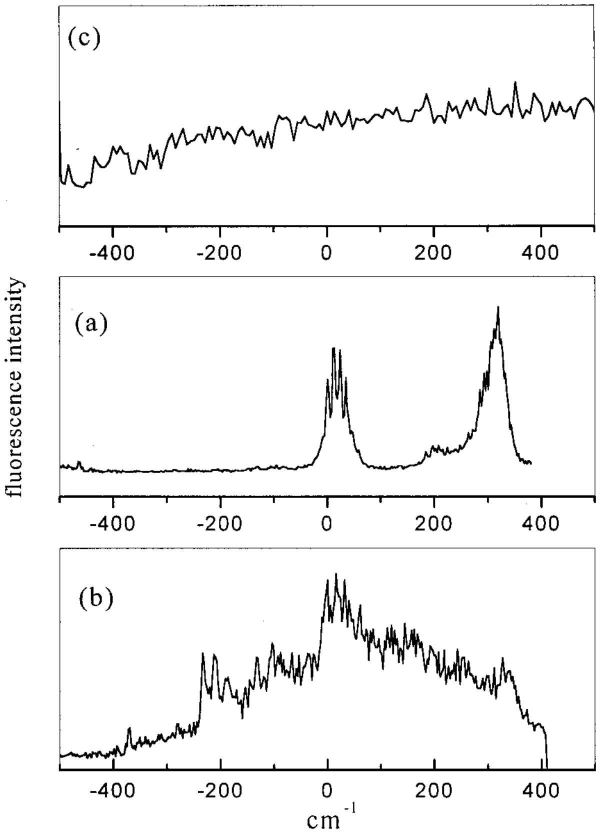


Figure 6. Fluorescence excitation spectra of MeO−Si−CN in the presence of CH_3CN: (a) bare molecule, (b) 1:1 complex with acetonitrile, and (c) larger clusters.

group, which lead to the stabilization of the LUMO as also shown by the lowering of the reduction potential of CN−Si relative to those of CN−C and benzonitrile in solution.[17]

Substitution by *tert*-butyl in electron donors such as DMA results in a moderate shift to the red (325 cm^{-1}), whereas the transition remains almost unaffected by TMS substitution (20 cm^{-1}). According to these findings, the L_b state of CN−Si lies at lower energy than that of CN−C, whereas the L_b transition of DMA−Si is higher in energy than that of DMA−C (see Figure 9).

It is also interesting to compare these data for the TMS and *tert*-butyl substituent effects on the S_0−S_1 (L_b) transition with those involving the second S_0−S_2 (L_a) transition. Because no information can be obtained from jet-cooled experiments, we refer to solution data, which show that the energy of the L_a state of benzonitrile is affected in a similar way by the presence of the TMS and *tert*-butyl groups in positions para to the CN group. On the other hand, the L_a state of the monomers of the donors (DMA and anisole) is almost not modified by substitution by a *tert*-butyl group, whereas substitution by TMS results in a redshift of about 2000 cm^{-1}: the charge-transfer character of the L_a state is enhanced by the *p*-silicon-containing substituent because of its electron-accepting properties. An obvious consequence of these observations is that the energy gap between the S_1 and S_2 states is much smaller in the Si-containing donor than that in the carbon-containing one.

No low-frequency mode (<100 cm^{-1}) has been observed in the excitation spectrum of the model compounds, apart from that of the dimethylamino derivatives, which shows that there is no strong modification of the geometry upon excitation along a coordinate involving the phenyl or methyl rotation. The DMA derivatives show the complicated vibrational pattern assigned to the coupled motion of the methyl groups.[27]

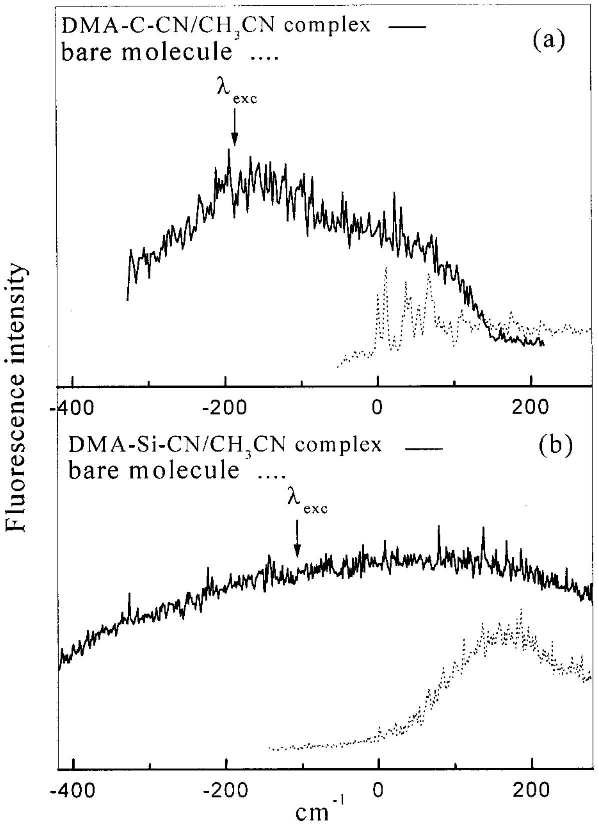


Figure 7. Effect of complexation with CH_3CN on the fluorescence excitation spectra of (a) DMA−C−CN and (b) DMA−Si−CN. The fluorescence is observed at λ (a) >345 and (b) >385 nm.

2. Bichromophores. All of the spectra except that of the compound MeO−C−CN can be interpreted in terms of a single conformation trapped in the jet. The isomerism observed in MeO−C−CN involves the orientation of the MeO substituent with respect to the diphenyl propane frame and does not infer that the relative conformation of the aromatic rings is different in the two conformers. Although we cannot rule out that the gas-phase geometry is different from that of the solid state, we can assume in a first approximation that for all of the bichromophores under study the planes of the two aromatic chromophores are perpendicular to each other, as observed for the crystal structure of compounds DMA−C−CN and DMA−Si−CN. However, this perpendicular geometry differs from the calculated and X- ray structures of diphenyl methane (CH_2 spacer), which show that the helical C_2 conformation corresponds to the minimum of the potential energy surface[28,29] and may be related to the steric restraints imposed by the presence of the methyl groups. The main difference between the Si-bridged compound and the C-containing one is the distance between the chromophores associated with the Si (bridge)−C (phenyl) bond distance being larger than that of the C (bridge)−C (phenyl) due to the size of the Si atom.

For the sake of clarity, the 0−0 transition energy of the compounds under study have been schematically drawn in Figure 9. The supersonic jet results reproduce the solution data despite minor changes due to solvation: the energy of the 0−0 transitions is redshifted in cyclohexane by about 300 cm^{-1}. The symmetrical species CN−C−CN and CN−Si−CN show a redshift of the 0−0 transition with respect to the corresponding model compound, which is larger for the carbon bridge (266 cm^{-1}) than for the silicon bridge (122 cm^{-1}). If it is assumed as shown experimentally that no strong electronic perturbation is introduced by the presence of the second benzonitrile unit,

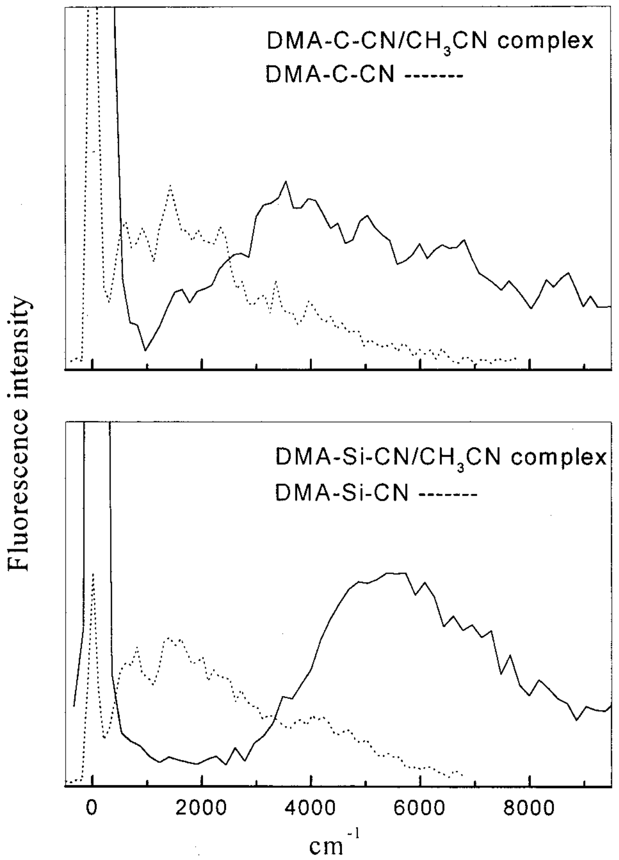


Figure 8. Effect of complexation with CH_3CN on the dispersed fluorescence of (a) DMA−C−CN and (b) DMA−Si−CN.

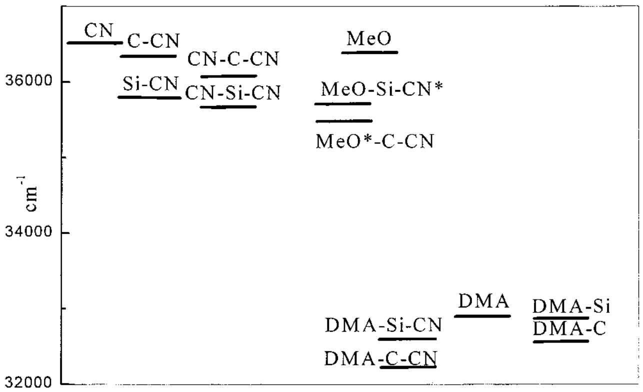


Figure 9. Comparative energy positions of the S_0−S_1 0−0 transitions of the bichromophores under study and of their model compounds.

this shift may be attributed to the increase of the dispersion energy between the two neighboring aromatic nucleus following excitation of one of the benzonitrile moieties. Because the CMe_2−C (phenyl) bond length is smaller than that of $SiMe_2$ −C (phenyl), the dispersion term of the interaction between both parts of the dimer is expected to be larger in the former case. Similar intramolecular dispersive interactions have been considered by van Dantzig et al.[6] to explain the shifts of 0−0 transitions in the case of perpendicular bichromophores involving substituted fluorenes.

According to what has been discussed above, substitution by *tert*-butyl maintains the relative energy order between benzonitrile and anisole excited states, because the one located on benzonitrile is expected to be redshifted by a slightly smaller amount than that located on anisole upon substitution by *tert*-butyl: the lowest excited state of MeO−C−CN indeed exhibits the characteristics of the anisole chromophore. On the other hand, substitution by TMS leads to a decrease of the transition energy of the benzonitrile chromophore larger than that of anisole. Thus, the replacement of the carbon spacer by the silicon one induces a level inversion: the lowest excited state of MeO−Si−CN is found to be localized on the benzonitrile moiety.

The dimethyl silylene bridge causes a low-frequency progression to appear in the region of the origin of CN−Si−CN and MeO−Si−CN and a broadening of this feature in DMA−Si−CN**.** This pattern is observed neither in the reference monomers Si−CN and DMA−Si nor in the corresponding diphenylpropanes. The vibrational modes involved are probably related to a hindered rotation of the phenyl−Si bond and their activity indicates a change between ground-state and excited-state geometries. The more simple structure observed in the spectra of the carbon-bridged compounds indicates that the carbon spacer gives more rigidity to the bichromophores and that the first L_b state has a geometry similar to that of the ground state. This observation may reflect either the larger flexibility of the silicon-containing molecules due to the increased distance between the aromatic rings or the hyperconjugative interaction between the σ orbitals of silicon−carbon bonds and the π orbitals of the benzene rings. The difference in hyperconjugation between ground and excited state would probably affect bond force constants coupled to the silyl substituent and thus the equilibrium geometries. A similar interpretation has been proposed in the case of phenylsilanes derivatives[30] where such low-frequency progressions are observed.

The general trends observed in this comparative study show that the spectroscopic properties of the isolated bichromophores are not strongly different from that of the corresponding monomers: the lowest fluorescent excited state corresponds to the ^1L_b state of the aromatic moiety which has the lowest energy S_1 state and which is not strongly perturbed by the presence of the second aromatic subunit. However, the dynamics of the excited state are affected by the spacer, as will be discussed below.

II. Electronic Coupling between Aromatic Moieties: Energy Delocalization. *1. Comparison between CN−C−CN and CN−Si−CN.* As mentioned previously, the origin of the CN−Si−CN excitation spectrum is followed by four bands which exhibit an odd/even alternance in the intensity distribution. The first hypothesis is that they correspond to a low-frequency mode whose potential energy surface displays a double minimum in the excited state, with the first vibrational level located above the barrier. A similar low-frequency structure has been observed in *p*-phenylpentamethydisilane[30] and *p*-cyanophenylpentamethyldisilane[18] and was suggested to be due to torsions of the phenyl group with respect to the $SiMe_2$ bridge, but no alternance in the intensity distribution was observed. Similar large amplitude motions can take place in CN−Si−CN because of reduced steric constraints for the rotation of the phenyl groups relative to CN−C−CN. However, it would be surprising if the barrier between the two minima was lower in CN−Si−CN than in *p*-phenylpentamethydisilane. Since the dispersed emission spectra of CN−Si−CN show that the two features separated by 25 cm^{-1} behave as two origins, we cannot exclude the possibility that they correspond to two 0−0 transitions separated by 25 cm^{-1}. Although the coexistence of two ground-state isomers cannot be ruled out, this result may also be interpreted as arising from an exciton splitting: the band located at 25 cm^{-1} of the most intense origin would thus correspond to the excitation of the second component of the mixed electronic state, and would be followed by the same 13 cm^{-1} vibration as the 0−0 band.

If we call ψ_a and ψ_b the wave functions of the two components of the exciton described in terms of the zeroth order excited state ψ_1 and ψ_2 localized on each subunit, and coupled by the off-diagonal matrix element β, we have

$$\psi_a = 1/\sqrt{2}(\psi_1 + \psi_2)$$

$$\psi_b = 1/\sqrt{2}(\psi_1 - \psi_2)$$

assuming that the chromophores are geometrically identical.

For a dipole-allowed transition, the coupling can be described to a first approximation by the dipole−dipole interaction, given by

$$\beta = \mu_1\mu_2\Gamma/4\pi\epsilon_0 R^3$$

where μ_1 and μ_2 are the transition dipole moments located on each benzonitrile moiety, Γ the orientation dependence of the interaction energy given by

$$\Gamma = \sin\Theta_a \sin\Theta_b \cos\Phi - 2\cos\Theta_a \cos\Theta_b$$

Θ_a and Θ_b are 54.5° and 125.5° because the aromatic rings are linked to a sp_3 atom. The transition moment has been deduced from the molar extinction coefficient ϵ obtained in cyclohexane solution and is 0.96 D. The distance between the centers of the dipoles is 5.4 A from crystallographic data in the solid state. The relative orientation between the transition moments of the two benzonitrile component can thus be estimated from the experimental exciton splitting $V = 2\beta = 25$ cm^{-1}, and is calculated to be $\Gamma = 0.41$.

According to this, the angle Φ between $\mu_1$and μ_2 is 79°. This value indicates that the geometry of the Si-containing molecule is slightly modified in the gas phase relative to the X-ray solid-state structure for which the two aromatic rings have been found to be orthogonal. A more distorted structure would be expected to allow a better overlap and thus a significant coupling between both subunits. We shall notice here that this value is compatible with the observed intensity ratio $I_+/I_- = 4$ between both components of the exciton splitting given by

$$I_+/I_- = (\vec{\mu}_+ + \vec{\mu}_-)^2 = (\vec{\mu}_1 + \vec{\mu}_2)^2/(\vec{\mu}_1 + \vec{\mu}_2)^2$$

2. Energy Transfer in MeO−Si−CN. In MeO−Si−CN, the lowest electronic excited state has been shown to be located on the benzonitrile moiety, and a second intense band 314 cm^{-1} higher in energy has been assigned to the excitation of the anisole chromophore, on the basis on its intensity. The dispersed fluorescence obtained by exciting this second feature is characteristic of the benzonitrile chromophore. This result can be interpreted in terms of a fast electronic energy transfer from the anisole moiety to the benzonitrile subunit, which takes place with about 300 cm^{-1} excess energy. It should be recalled as mentioned in the experimental results that a weak vibrational band is observed at this energy in the **Si**−CN monomer. Thus, electronic interactions responsible for the transfer can be promoted by the resonant coupling between two almost isoenergetic manifolds. The large density of vibrational states provided by the numerous low-frequency modes ensures the irreversibility of the process and explains that no fluorescence from the anisole donor is observed. A similar mechanism was proposed by Levy's group to explain the energy transfer occurring in perpendicular spirobifluorenes and derivatives.[6,7] Despite the fact that no electronic coupling was expected to take place at the zero level in these compounds because of the geometry, efficient energy transfer was observed and was explained in terms of vibronic coupling between the sparse states of the donor and the dense manifold of the acceptor. It should be noticed that the broadening of the low-frequency structure observed here provides a further argument for a strong coupling between the two chromophores excited states: the rate of energy transfer can be estimated from the observed broadening to be a few or a few tens of picoseconds.

In MeO−C−CN, the first electronic transition is located on the anisole moiety. As the S_1 states of the anisole and benzonitrile chromophore are very close in energy (130 cm^{-1} in the non substituted molecules), one could expect to observe the excited state localized on benzonitrile in close proximity: thus an energy transfer process, with anisole acting as an acceptor and benzonitrile as a donor may take place. However, one also has to consider the oscillator strength of the transition which is larger by a factor of 4 in anisole than in benzonitrile when substituted by the *tert*-butyl group. Such a localized excitation on the benzonitrile chromophore would be difficult to identify in the spectrum of MeO−C−CN because its intensity is expected to be weak and of the same order as the vibronic features of the lowest excited state localized on the anisole chromophore.

The results obtained for MeO−Si−CN indicate that the electronic energy transfer is very fast. This can be related to the short distance between the donor and the acceptor: In a similar bichromophore which contains *p*-xylene as a donor linked by a three-membered chain to *o*-xylene as an acceptor, the energy gap between the donor and the acceptor is almost the same as in MeO−Si−CN (294 cm^{-1}). However, the dual fluorescence (both acceptor and donor-like) observed when exciting the donor shows that the transfer is not complete, because of the large distance between the donor and the acceptor.[31] On the other hand, the low-frequency progression observed in the excitation spectrum of MeO−Si−CN shows that the modification of its geometry upon excitation must be important and that the perpendicular geometry assumed in the ground state is not maintained anymore in the excited state. This favors the coupling between transition moments if the approximation of a dipole−dipole mechanism holds for energy transfer (Förster mechanism), or the overlap between the π aromatic orbitals of the aromatic subunits if an exchange Dexter type mechanism is involved.

III. Charge-Transfer Process in Donor (DMA)−Acceptor (Benzonitrile) Bichromophores: Comparison with Solution.

1. Isolated Molecules. While the fluorescence excitation spectrum of DMA−C−CN shows exactly the same vibrational structure as that of the DMA model compound, the excitation spectrum of DMA−Si−CN displays a much broader and congested structure. The shape of this band is reminiscent of the spectra observed in the donor−acceptor complexes involving anthracene and dimethylaniline[10] or some donor-bridge-acceptor compounds[2] and might be attributed to a mixing of the locally excited state with a close lying CT state. However, no redshifted emission characteristic of a charge-transfer state has been observed when exciting this broad feature. The broadening of the absorption is thus probably due to spectral congestion resulting from the combination of the vibrational pattern associated with the dimethylamino group with the low-frequency torsions of the aryl groups with respect to the $SiMe_2$ spacer as seen in MeO−Si−CN. This shows that the geometry of DMA−Si−CN is much more modified upon excitation than that of DMA−C−CN**.** The moderate Stokes shift of about 2000 cm^{-1} can be related to a displaced Franck−Condon distribution in the locally excited state of the DMA chromophore. This conclusion diverges from the previous statement deduced from the absorption spectra in solution: the increase of the absorption in the region below 35000 cm^{-1} as observed in cyclohexane has been assigned to the direct absorption to a charge-transfer state from which fluorescence takes place. The presence of a low-lying CT state in these molecules was further confirmed by solvatochromism and microwave conductivity studies which show a large value of the excited-state dipole moment (about 18 D) for both donor−acceptor bichromophores. The energy of the CT state in the gas phase can be estimated from the following equation:

$$E_{CT} = IP_D - EA_A - e^2/R_{DA}$$

where IP_D is the ionization potential of the donor (7.1 eV for dimethylaniline[32] and 8.2 eV for anisole) EA_A is the electronic affinity of benzonitrile (0.25 eV[33]). Although the last term is only an approximation resting on the hypothesis of point charges, the Coulombic interaction in the D^+- A^- pair can be in a first approximation calculated to be 2.665 eV for the Si spacer with $R_{DA} = 5.4$ A and 2.937 eV for the C spacer with $R_{DA} = 4.9$ A. As a result of the larger distance, the CT state of CN−Si−DMA is expected to lie at higher energy than that of CN−C-DMA. However, it has been shown from the half wave redox potentials determined in solution, that the presence of a trimethylsilyl or dimethylphenylsilyl substituent in *para* position of benzonitrile or dimethylaniline modifies their redox properties and may compensate the difference in the Coulombic term. When taking these corrections into account, the CT states of both compounds are calculated to be very close in energy (∼4 eV). Furthermore, the photoinduced CT process is found to be slightly endothermic for DMA−Si−CN as well as DMA−C−CN. Thus, in both cases the electron transfer process is thermodynamically forbidden in the jet-cooled bare molecules and this explains why the lowest fluorescent state is the first ^1L_b state localized on the dimethylaniline moiety. Because IP_D of anisole is 1 eV higher than that of DMA, the CT state of MeO−Si−CN is expected to lie at much higher energy than the first excited state.

2. Complexes with CH3CN. In contrast with the bare molecules, a Stokes shifted charge-transfer emission is observed when DMA−C−CN, DMA−Si−CN and MeO−Si−CN are clustered with acetonitrile. A continuous absorption appears in the region of the S_0−S_1 transition from which a redshifted emission takes place: this result indicates that solvation with a polar partner is required to induce the CT formation. In the case of MeO−Si−CN, no redshifted emission is observed for the 1:1 complex and solvation of MeO−Si−CN by a larger number of acetonitrile molecules is necessary to stabilize the charge-transfer state. Because the ionization potential of DMA is smaller than that of anisole, photoinduced charge transfer occurs in 1:1 complexes of both DMA−C−CN and DMA−Si−CN.

However the spectroscopic properties of the complexes of DMA−C−CN and DMA−Si−CN differ from one other: the excitation spectrum is much broader and intense for the Si-containing species than for the carbon analogue and the Stokes shift of the emission is much larger for DMA−Si−CN than for DMA−C−CN. These two observations refer to different processes: the energy of the redshifted emission relates to the Franck Condon transition from the CT to the S_0 ground state, while the excitation spectrum involves the vertical transition from the ground-state geometry toward the first excited state of the complex.

We shall first discuss the effect of complexation by acetonitrile on the broadening of the excitation spectra of the bichromophores. The continuous absorption observed for both systems is typical of a strong coupling between the optically excited L_b state and a close lying charge-transfer state. A larger bandwidth is observed for DMA−Si−CN, which reflects the properties of the bare molecule, namely a more displaced Franck−Condon window in DMA−Si−CN than in DMA−C−CN. A strong fluorescence enhancement has been observed for both complexes. This shows that the quantum yield of fluorescence is increased by complexation. A similar increase has been observed in solution for solvents of medium polarity. The enhanced fluorescence has been related to a larger radiative character for the transition at play in polar solvents and has been rationalized in terms of the coupling of the CT state with the L_a state which bears a large oscillator strength, and from which the transition probability is borrowed. Despite our experiments not allowing us to know whether the radiative or nonradiative rate constants are responsible for this effect, the same explanation may hold in the complex with acetonitrile.

The enhanced fluorescence observed in jet cooled complexes contrasts however with the results in acetonitrile solution[17] which have shown that the quantum yield of the CT type emission is very low (0.0015). The difference between solution-phase behaviors and what is observed here in 1:1 complexes can be explained in the following way: in a medium of high polarity, the CT transfer state is strongly stabilized and evolves to a pure CT state consisting of an intramolecular ion pair which is, in most cases, non fluorescent. Because the energy gap between the CT state and the higher energy LE states is increased, the mixing with the allowed ^1L_a state, from which transition probability is borrowed, decreases. Such a process can be responsible for the low radiative rate constant observed in acetonitrile solutions of DMA−Si−CN or DMA−C−CN relative to other solvents. It is likely that in the 1:1 complex the vertical excitation leads to a state with a large mixed LE and CT character responsible for the intense redshifted fluorescence whereas in solution the ion-pair character prevails.

The most puzzling point is the 2000 cm^{-1} energy difference in the charge-transfer emission maximum in the silicon-bridged compound relative to that of the carbon-containing one. As the observed Stokes shifted fluorescence corresponds to a transition from the CT state toward the repulsive part of the ground-state surface, this difference may have two origins. The first one is that emission takes place from a lower CT state in DMA−Si−CN than in DMA−C−CN. The second one is that the more redshifted emission obtained for DMA−Si−CN is due to the emission toward a more repulsive part of the ground-state energy surface, if the geometry of the emitting CT state differs more from that of the ground state for DMA−Si−CN than that for DMA−C−CN.

A similar difference has been observed in solution and has been related to the lowering of the reduction potential of the benzonitrile subunit by the silicon bridge. However, as discussed previously, this effect is counterbalanced by the increased Coulombic term so that the energy of the CT states of isolated DMA−C−CN and DMA−Si−CN are expected to be located at similar energy. Furthermore, because the excited dipole moments of both compounds have been determined by solvatochromic and microwave conductivity methods to be of the same order (19−20.5 D), complexation with a polar solvent such as acetonitrile is expected to stabilize by a similar amount the D^+−C−A^- and the D^+−Si−A^- species, and the CT state of the complex of the silicon-containing compound should still lie at an energy similar to that of the carbon-containing one.

It seems thus more likely that the reason for a larger redshift in the case of DMA−Si−CN is the modification between the geometry of the ground and the charge-transfer states. This parallels the complicated vibrational structure that is observed in the S_0−S_1 excitation spectrum of the bare molecules.

Conclusions

The photophysical properties of a series of diphenyl propanes and diphenyldimethylsilanes have been examined in the isolated gas phase and compared with their behavior in solution. The Si spacer, while keeping the two chromophores further apart with respect to the C spacer, is shown to induce a distortion of the excited state that allows a larger coupling between the aryl components. The ability of the silicon bridge to mediate electronic coupling results in a delocalization of the electronic energy in CN−Si−CN and MeO−Si−CN. An exciton splitting has been suggested to take place in the symmetrically substituted bichromophore, and a fast electronic energy transfer from the anisole donor to the benzonitrile acceptor has been observed in MeO−Si−CN. In both DMA−C−CN and DMA−Si−CN molecules, no electron transfer takes place in isolated conditions for thermodynamical reasons. Solvation by CH_3CN results in a Stokes shifted emission, demonstrating that charge migration takes place in both systems. The CT emission is more displaced toward low energy for the silicon-containing bichromophore than that for the carbon-containing one. These results suggest that the conformational changes are much more important in the silicon-containing species.

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