# Conformational Dynamics of Flexibly and Semirigidly Bridged Electron Donor-Acceptor Systems As Revealed by Spectrotemporal Parameterization of Fluorescence

I. H. M. van Stokkum\*

Faculty of Physics and Astronomy, Free University, De Boelelaan 1081, NL-1081 HV Amsterdam, The Netherlands

## T. Scherer,\* A. M. Brouwer, and J. W. Verhoeven

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, NL-1018 WS Amsterdam, The Netherlands

Received: August 5, 1993; In Final Form: November 5, 1993\*

Conformational changes of intramolecular charge-transfer (CT) species were studied by means of time-resolved fluorescence spectroscopy. From a time-resolved fluorescence spectrum the parameters which describe a kinetic, compartmental model as well as the fluorescence spectral-shape parameters were estimated. The systems (Chart 1) differed in donor and acceptor strengths and possessed two different kinds of bridges: a flexible trimethylene chain and a semirigid piperidine ring. In moderately polar solvents ( $\epsilon > 3.5$ ) only fluorescence originating from an extended dipolar species (extended charge transfer (ECT) state) was found, possessing a dipole moment of about 27 D. In low dielectric media the systems with a strong cyanonaphthalene acceptor showed "harpooning": the ECT species was converted to a folded dipolar species (contact charge transfer (CCT) state), similar to a tight polar exciplex, on a time scale of less than 1 ns (flexible bridge) or 7 ns (semirigid bridge). No indications were found for an ECT in the systems with a weak naphthalene acceptor in nonpolar solvents. Semirigidly bridged systems displayed only local fluorescence, whereas in the flexibly bridged systems CT fluorescence originating from two types of CCT was found instead.

## 1. Introduction

The electronic structure of exciplexes between species with electron donor (D) and electron acceptor (A) properties can be described by taking into account a large contribution of a configuration, D<sup>+</sup>A<sup>-</sup>, in which one electron has been transferred from D to A (e.g., ref 1). In many cases fluorescence can be observed from such species (D<sup>+</sup>A<sup>-</sup> $\rightarrow$  DA +  $h\nu$ ). A characteristic feature of this charge-transfer (CT) emission is its high sensitivity to the polarity of the solvent: as a result of the large dipole moment the energy of the exciplex is lower in more polar media, which leads to a progressive red shift of the emission with increasing polarity.

It has long been thought that a prerequisite for exciplex emission is "direct contact", spatial overlap between molecular orbitals of D and A. It is indeed likely that, in nonpolar media, where the electrostatic attraction between the oppositely charged fragments is large, exciplexes exist as contact ion pairs. As Weller pointed out<sup>2,3</sup> dissociation of the contact ion pair into a solvent-separated ion pair, and ultimately into free ions, is favorable in media of moderate polarity, typically with dielectric constants greater than about 8. Under these circumstances the competition between electrostatic attraction and solvation energy (which is greater for free ions) is won by the latter.

The question of whether CT or exciplex fluorescence can only occur in contact ion pairs has long been the subject of lively debate. A change in the electronic structure of the exciplex with increasing solvent polarity (as a result of an admixture of the ground-state wave function) has been inferred from the decrease of the radiative rate constant. Moreover, Mataga et al.<sup>4</sup> provided evidence for an increase with solvent polarity of the average D–A distance in the emissive state of polar exciplexes, a view strongly militated against by the Weller group.<sup>2,5</sup> Especially for intramolecular systems where D and A are linked by a flexible polymethylene bridge (D–(CH<sub>2</sub>)<sub>3</sub>–A), it was concluded that the exciplex geometry was changed from "compact" in nonpolar media to "loose" in polar media.<sup>6-10</sup> Furthermore, evidence was found in time-resolved absorption and fluorescence studies that in polar media (2-propanol, acetone, and acetonitrile) a compact "sandwich" species was formed from an extended loose species on a time scale of 0.9–1.2 ns.<sup>9,11-14</sup>

Inspired by the fact that bridged systems could provide more insight into exciplex (and excimer) geometries of intramolecular D-A systems, and given the conformational complexities of flexible polymethylene-bridged systems, attention was focused upon systems with better defined geometries.<sup>15-19</sup> In these systems D and A are separated by rigid saturated hydrocarbon spacers, not allowing spatial overlap between the chromophores. It was shown that efficient photoinduced intramolecular charge separation can still occur across these bridges. Several of these systems were found to display exciplex-like emission,<sup>15-19</sup> and therefore it was concluded that a close contact or compact conformation is not an exclusive condition for charge separation in bichromophoric systems nor for the observation of "exciplex" emission. The latter strongly supports the view as expressed originally by Mataga.<sup>6,8-12,20</sup>

More recently<sup>21,22</sup> an example of a change in exciplex structure in low-polarity media was most convincingly demonstrated for a semirigidly bridged system. Although the possibility of longrange electron transfer prior to extensive conformational reorganization in these media for strong D-A combinations was already recognized as early as 1978,<sup>23</sup> the first example which provided direct evidence of this "harpooning mechanism" was given in 1990 by Wegewijs et al.<sup>22</sup> soon after the discovery of this process in the gas phase under molecular beam conditions.<sup>21</sup> It was shown that an anilino-4-cyanonaphthalene system linked by a 4-substituted piperidine moiety as a spacer with intermediate flexibility can undergo an enormous conformational change after photoinduced charge separation due to the Coulombic force. Thus, time-resolved fluorescence and microwave conductivity measurements indicated that the exciplex in nonpolar solvents is preceded by a totally different CT state with a much larger dipole

<sup>•</sup> Abstract published in Advance ACS Abstracts, January 1, 1994.



moment, which nevertheless emits "exciplex-like" CT fluorescence. In the low dielectric media, this initial extended charge transfer (ECT) conformation is thus rapidly followed by an interconversion to a folded contact charge transfer (CCT) conformation at room temperature. The latter species emits its CT fluorescence at longer wavelengths than the extended precursor. Later other systems were found to behave similarly.<sup>24,25</sup>

The "harpooning process" is limited to low-polarity solvents (where the electrostatic energy dominates the solvation energy) and strong D-A couples, which allow long-range electron transfer to be energetically feasible in such low-polarity media. The low rotational barriers in flexible polymethylene chains make it difficult to discriminate among possible CT emissions from different conformations, whereas completely rigid systems obviously lack such changes. Therefore, a possible gradual change in the exciplex structure as a function of solvent polarity can probably best be studied by comparison of differently bridged systems with (nearly) identical electronic properties. This approach was followed by us recently<sup>26</sup> for several typical D-A pairs in semirigidly and flexibly bridged and nonbridged arrangements. Steady-state fluorescence measurements revealed that the structure of emissive polar exciplexes between separate or flexibly bridged D and A species may change considerably in response to solvent polarity, from a CCT-type structure in nonpolar media to an ECT-type structure in polar media.<sup>26</sup> In this paper we want to go into more detail by using a critical analysis of time-resolved fluorescence spectra to study solvent effects upon CT emission and upon exciplex lifetimes for D-A pairs that are flexibly or semirigidly bridged. The molecules studied consist of a photoexcitable (4-cyano)naphthalene electron acceptor, an aromatic amine electron donor, and a bridge interposing three saturated C atoms. We distinguish the molecules (Chart 1) by a two-letter and one-digit code. The donor can be either "strong" (S, 4-methoxyaniline) or "weak" (W, aniline). Likewise 4-cyanonaphthalene and naphthalene are, respectively, strong and weak acceptors. Three types of bridges are investigated: 1, a flexible trimethylene chain; 2, a piperidine ring; and 3, a piperidine ring with a cyano group at the bridgehead carrying the acceptor.

The redox potentials of the chromophores determine the energies of the CCT and ECT configurations relative to the locally excited state (DA<sup>+</sup>). For the systems studied here three typical cases are distinguished.<sup>26</sup>

(I) Weak D-A pairs (WW and SW series) in nonpolar solvents: the flexibly bridged systems WW1 and SW1 display CT emission which typically arises from a CCT species. Such a folded charge-separated conformation is severely hampered for the piperidine-bridged counterparts WW2 and SW2, as the piperidine ring adopts a chair conformation with both aromatic substituents in equatorial positions. From the lack of CT fluorescence for both WW2 and SW2 it is concluded that these D-A pairs are not strong enough to induce electron transfer and therefore cannot create an ECT species.

(II) Weak and strong D-A pairs in polar solvents: by increasing solvent polarity, both the CCT and ECT states become ther-

modynamically accessible. Despite the decreased Coulombic stabilization, the stronger solvation of the ECT results in a preference for an ECT configuration.

(III) Strong D-A pairs (WS and SS series) in nonpolar solvents: long-range electron transfer is made feasible, because the strong D-A pair has decreased the ECT state below the locally excited state. Upon photoexcitation the bridged molecule when in an extended conformation can thus rapidly form an ECT species, but this extended species collapses into a thermodynamically more favorable CCT species due to the huge Coulombic attraction in nonpolar solvents.

We have recently started to study several cases where the dynamics of fluorescence could be employed to monitor conformational changes (in particular upon "harpooning"). This was done by applying kinetic models and spectral shape models to different sets of nanosecond time-resolved fluorescence data obtained using a time-gated optical multichannel analyzer, which provides a high spectral resolution.<sup>25</sup> To complement the low time resolution (5 ns) of these data, fluorescence decays were now also measured at a small number (typically 12) of wavelengths. Furthermore, in a small number of cases the influence of temperature upon the fractional yield of harpooning was studied by measuring steady-state emission spectra.<sup>26</sup> By means of timeresolved spectroscopy the kinetics of a mixture of components whose spectra overlap can be measured indirectly by observing the total spectrum at several time instants. The perfect, noisefree, time-resolved spectrum  $\psi$  is a superposition of the contributions of the  $n_{\rm comp}$  different components:

$$\psi(t,\lambda) = \sum_{l=1}^{n_{\text{comp}}} c_l(t) \ \epsilon_l(\lambda) \tag{1}$$

where  $c_i(t)$  and  $\epsilon_i(\lambda)$  denote, respectively, the concentration and emission spectrum of component l. Measurement of  $\psi$  poses the inverse problem: how can the spectroscopic and kinetic properties of the components be recovered? We will determine the number of components from the data, estimate the kinetic parameters using a compartmental model, and estimate the parameters that describe the spectra. Models with differential equations that are linear in the concentrations (like first-order chemical reactions) are termed compartmental models.<sup>27,28</sup> A complication is that different compartmental models with the same kinetic parameters result in identical residuals (for proof see, e.g., ref 25). These models differ only in their accompanying spectral parameters. Thus, a priori knowledge about the spectra is necessary to choose between different candidate models. One can use the fact that the fluorescence intensity cannot be negative, but one could also make use of spectral shapes which are a priori supposed or independently measured on appropriate reference compounds. The results of the parameter estimation consist of a kinetic model with estimated rate constants as well as the (shapes of the) fluorescence emission spectra of the components, enabling us to investigate solvatochromic shifts, viscosity effects, and the harpooning process.

TA	BLE	1: 1	Prope	rties (	of Solvents	(20 °C):	Polarity	$\Delta f$ (See
Eq	13),	Visco	osity 7	), and	Dielectric	Constant	e	

solvent	$\Delta f$	η (cP)	£
2-methylbutane	0.091	0.225	1.843
n-hexane	0.092	0.3126	1.890
n-nonane	0.098	0.716	1.972
cyclohexane	0.100	0.980	2.023
methylcyclohexane	0.100	0.734	2.02
<i>n</i> -tetradecane	0.102	2.33	2.036
n-hexadecane	0.103	3.44	2.051
trans-decalin	0.110	2.128	2.172
cis-decalin	0.111	3.381	2.197
di-n-hexyl ether	0.170		2.77ª
di-n-pentyl ether	0.171	1.08	2.774
di-n-butyl ether	0.194	0.69	3.08
di-n-propyl ether	0.213	0.42	3.394
diisopropyl ether	0.237	0.33	3.98
diethyl ether	0.251	0.23	4.34
n-butyl acetate	0.267	0.73	5.01
ethyl acetate	0.292	0.46	6.00
tetrahydrofuran	0.308	0.49	7.58
dichloromethane	0.319	0.44	9.08
1-butanol	0.361	2.95	17.8
ethanol	0.379	1.20	25.0
acetonitrile	0.393	0.36	37.5

<sup>a</sup> At 25 °C.

### 2. Methods

2.1. Experimental Details. The preparation of the compounds will be described elsewhere. The solvents used were (in order of the solvent polarity parameter  $\Delta f$ , eq 13; see Table 1) 2-methylbutane (Aldrich spectro), n-hexane (Merck Uvasol), n-nonane (Aldrich p.a.), cyclohexane (Merck Uvasol), n-tetradecane and n-hexadecane (Aldrich p.a.), methylcyclohexane (Aldrich spectro), trans-decalin and cis-decalin (Merck p.a. or Fluka), di-nhexyl ether and di-n-pentyl ether (Aldrich), di-n-butyl ether (Merck or Fluka), di-n-propyl ether (Fluka), diisopropyl ether (Merck), diethyl ether (Merck Uvasol), n-butyl acetate (Aldrich spectro), ethyl acetate, tetrahydrofuran and dichloromethane (Merck Uvasol), 1-butanol (Merck p.a.), ethanol (Merck Uvasol), and acetonitrile (Merck p.a.). The decalins and ethers were purified by the usual procedures.<sup>29</sup> The solutions had an absorbance of about 0.1 in 1 cm at 308 nm and were deoxygenated by purging with argon for at least 15 min.

For excitation of the samples at 308 nm a Lambda-Physik EMG 101 XE/HCl excimer laser was used which produces pulses with an essentially Gaussian time profile with a width (fwhm) of about 7 ns and an energy of 5-10 mJ/pulse. The laser was operated at a rate of 2-5 Hz. In some experiments we used a Lumonics 748 excimer laser or 315-nm excitation derived by frequency doubling the output of a Spectra Physics PL-1 dye laser (DCM dye) pumped at 532 nm by a Q-switched Nd-YAG laser (Spectra Physics Quanta Ray GCR-3). Fluorescence was detected at a right angle and collected by an optical fiber which led to a Jarrell-Ash monospec 27 Model 1234 spectrograph in which the light was dispersed by a grating (150 grooves/mm) onto an MCP intensified diode array detector (EG&G 1421G, 25 mm, 1024 diodes). With this setup a spectral range of about 600 nm was covered with a bandwidth of 5 nm (25- $\mu$ m entrance slit) or 7 nm (250- $\mu$ m slit). The detector was gated with a width of 5 ns by an EG&G 1302 pulse generator. The timing of the laser and optical multichannel analyzer (OMA) gate pulse was controlled by the EG&G OMA III Model 1460 console with a 1303 pulse delay generator and a digital delay generator (EG&G Model 9650).

Each experiment involved recording spectra at 15-45 different time instants with a constant time increment. At each time point spectra from 10-20 shots were averaged. In order to allow the experiment to be extended over a sufficiently large number of laser shots, without degradation of the sample, the laser pulse power was attenuated by means of neutral density filters. The spectral intensities were not corrected for the wavelengthdependent response of the detection system.

Decays at single wavelengths were recorded using a transient digitizing system as described elsewhere<sup>30</sup> using a binwidth of 0.2 or 0.4 ns.

Steady-state fluorescence spectra were recorded on a Spex Fluorolog II emission spectrometer, using an excitation wavelength of 300 nm. Quantum yields were obtained by determining the fluorescence intensity integrated from 310 to 700 nm of the sample relative to the integrated fluorescence intensity of 9,10-diphenylanthracene ( $\Phi = 0.9$ ) determined at the same excitation wavelength in cyclohexane. Quantum yields determined in other solvents were corrected for changes in the refractive index in the solvent compared to cyclohexane.<sup>31</sup> For the low-temperature measurements an Oxford Instruments liquid nitrogen cryostat DN 1704 (with an ITC 4 control unit) was used. The solutions were degassed via four freeze-pump-thaw cycles on a highvacuum line.

The reduction and oxidation potentials of the systems studied together with the separate chromophores were determined by cyclic voltammetry using a Bank Electronic POS 73 Wenking Potentioscan coupled to a HP 7090A measurement plotting system.<sup>32</sup> Measurements were carried out in DMF solution with tetraethylammonium fluoroborate (0.1 M) as electrolyte and at sweep rates of 100–400 mV/s. A platinum working electrode with a platinum gauze auxiliary electrode was used in combination with a saturated calomel reference electrode (SCE).

2.2. Theoretical Details. The basic model which describes the time evolution of spectra is the following (notation convention: underlining indicates stochastic variables, uppercase represents matrices, lowercase represents scalars or vectors, and a circumflex indicates an estimator):

$$\underline{\psi}_{t_i\lambda_j} = \sum_{l=1}^{n_{\text{comp}}} c_{lt_i}\epsilon_{l\lambda_j} + \underline{\xi}_{t_i\lambda_j}$$
(2)

$$\underline{\Psi} = \mathbf{C}\mathbf{E}^{\mathrm{T}} + \underline{\Xi} \tag{3}$$

where the  $m \times n$  matrix  $\Psi$  denotes the measured time-resolved spectra, measured at *m* time instants  $t_i$  and *n* wavelengths  $\lambda_j$ .  $c_{li_l}$ denotes the concentration of component *l* at time  $t_i$ ,  $\epsilon_{l\lambda_j}$  denotes the emission of component *l* that occurs at wavelength  $\lambda_j$ , and  $\xi_{i,\lambda_j}$  denotes a Gaussian distributed stochastic disturbance with zero mean. The  $c_{li_l}$  and  $\epsilon_{l\lambda_j}$  are gathered in the matrices **C** and **E**, of dimensions  $m \times n_{comp}$  and  $n \times n_{comp}$ , respectively. Matrix  $\Xi$ is, like  $\Psi$ ,  $m \times n$ .

Regarding eq 2, we note that the quantity which will be estimated is the product  $c_{f_{\epsilon}}^{T}$  which in itself is insufficient for the determination of the absolute values of  $c_{l}$  and  $\epsilon_{l}$ .

**2.2.1.** Estimation of the Number of Components. In general, rank(C) = rank(E) =  $n_{comp}$ , and with perfect, noise-free data ( $\Xi = 0$ ) we have rank( $\Psi$ ) = rank(CE<sup>T</sup>) =  $n_{comp}$ . Thus, with experimental data of which we do not know the number of components it is necessary to estimate the rank of  $\Psi$ .

We estimate this rank using the singular value decomposition of  $\underline{\Psi}$ :

$$\Psi = \underline{\mathbf{USW}}^{\mathrm{T}} \tag{4}$$

where U and W are orthogonal matrices, respectively  $m \times m$  and  $n \times n$ , whose columns contain the left and right singular vectors. S is an  $m \times n$  matrix which is zero except for its diagonal, which contains the singular values. With  $n_{\text{comp}}$  components and noise-free data we have exactly  $n_{\text{comp}}$  significant singular values:  $s_1 \ge s_2 \ge ... \ge s_{n_{\text{comp}}} > s_{n_{\text{comp}}} + 1 = ... = 0$ .

**2.2.2.** Estimation of Spectral and Kinetic Parameters. Let us assume in the following that we have successfully determined  $n_{\text{comp}}$ . We now consider three different kinds of parameterizations.

(i) The concentrations are described by a kinetic model, which depends upon the nonlinear parameters  $\theta$ , whereas the spectral parameters of the  $n \times n_{\text{comp}}$  matrix E are simply linear parameters:

$$\Psi = \mathbf{C}(\theta)\mathbf{E}^{\mathrm{T}} + \Xi \tag{5}$$

(ii) The spectra are described by a parametric model, which depends upon the nonlinear parameters  $\theta$ , whereas the concentration parameters of the  $m \times n_{comp}$  matrix C are simply linear parameters:

$$\Psi^{\mathrm{T}} = \mathbf{E}(\theta)\mathbf{C}^{\mathrm{T}} + \Xi^{\mathrm{T}}$$
(6)

(iii) Both the concentrations and the spectra are described by a model, which depends upon the nonlinear parameters  $\theta$ . Assuming first-order kinetics, a matrix of linear parameters A describes the concentrations of the components in terms of a superposition of simple decays which are gathered in the matrix  $C(\theta)$ .

$$\Psi = \mathbf{C}(\theta)\mathbf{A}\mathbf{E}^{\mathrm{T}}(\theta) + \Xi$$
(7)

The linear parameters (E in eq 5, C in eq 6, A in eq 7) can be eliminated in the nonlinear least-squares fit.<sup>25,33-35</sup>

**2.2.3.** Compartmental Models. In a linear compartmental model<sup>27,28</sup> the differential equation for the concentrations is

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{c}(t) = \mathbf{K}\mathbf{c}(t) + \mathbf{j}(t) \tag{8}$$

where c and j are  $n_{\text{comp}} \times 1$  vectors:  $\mathbf{c} = [c_1, ..., c_{n_{\text{comp}}}]^T$ ,  $\mathbf{j}(t) = i(t)[1, x_2, ..., x_{n_{\text{comp}}}]^T$ , where i(t) is the result of a convolution of the exciting laser pulse and the detector response, and  $x_l$  represents a possible extra input to compartment l. We assume that all eigenvalues of the transfer matrix **K** are different, and that  $\mathbf{c}(-\infty) = 0$ .

The solution of eq 8 is given by  $c(t) = e^{Kt} \oplus j(t)$  where  $\oplus$ indicates convolution. For a diagonal K matrix (K = diag( $\kappa_1, ..., \kappa_{n_{comp}}$ ), where  $\kappa = -k$  is an eigenvalue) the concentration matrix C consists of elements  $[C_1]_{pq} = c_q^I(t_p, k_q, \mu)$ , where  $\mu$  is a parameter describing the time shift relative to the system response i(t). The solution of the general compartmental model is a linear combination of the  $c_l^1$  and thus a transformation of  $C_1$  (derived from the eigenvalues of the transfer matrix K) for which we can write  $C_{II} = C_1 A_{II}$ . An example can illustrate this: suppose we have two independent exponential decays  $c_i^I(t) = e^{-k_i t}$  (i = 1, 2) with accompanying decay associated spectra (DAS)<sup>36,37</sup>  $\epsilon_l^I(\lambda)$ . Then model II where component 2 is formed from component 1 with fractional yield  $\Phi_{12}$  is described by the linear combination

$$c_{1}^{I}(t) \epsilon_{1}^{I}(\lambda) + c_{2}^{I}(t) \epsilon_{2}^{I}(\lambda) = c_{1}^{I}(t)(\epsilon_{1}^{I}(\lambda) + \epsilon_{2}^{I}(\lambda)) + (c_{2}^{I}(t) - c_{1}^{I}(t))\epsilon_{2}^{I}(\lambda)$$
(9)

Thus,  $c_1^{II}(t) = c_1^{I}(t)$ ,  $\epsilon_1^{II}(\lambda) = \epsilon_1^{I}(\lambda) + \epsilon_2^{I}(\lambda)$ ,  $c_2^{II}(t) = \alpha(c_2^{I}(t) - c_1^{I}(t))$ , and  $\epsilon_2^{II}(\lambda) = \epsilon_2^{I}(\lambda)/\alpha$ , where  $\alpha = \Phi_{12}k_1/(k_1 - k_2)$ . In words, the differences between the two models are that the concentration of the formed component is proportional to the difference between the two decays, whereas the spectrum of the precursor is the sum of the two DAS. The other way around,

$$\epsilon_1^{\rm I}(\lambda) = \epsilon_1^{\rm II}(\lambda) - \alpha \epsilon_2^{\rm II}(\lambda) \tag{10}$$

Thus, the DAS of the precursor can contain negative amplitudes when the kinetics obey model II.

**2.2.4.** Spectral Model. The shape of a charge-transfer fluorescence emission spectrum is often well described by a Gaussian in the energy domain:<sup>38</sup>  $f(\bar{\nu})/\bar{\nu}^3 = f_{\max} \exp(-\ln 2[2(\bar{\nu} - \bar{\nu}_{\max})/\Delta\bar{\nu}]^2)$  where  $\bar{\nu} = \lambda^{-1}$  denotes the wavenumber and  $f(\bar{\nu})$  is the converted fluorescence emission spectrum,  $f(\bar{\nu}) = \lambda^2 \epsilon(\lambda)$ .<sup>39</sup> The wavenumber of maximum emission is denoted by  $\bar{\nu}_{\max}$ , whereas  $\Delta\bar{\nu}$  is the fwhm. Even better fits are achieved when an extra skewness parameter is introduced.<sup>40,41</sup> Thus, we arrive at

the model function

$$\epsilon(\tilde{\nu}) = \tilde{\nu}^{5} f_{\max} \exp(-\ln 2[\ln(1+2b(\tilde{\nu}-\tilde{\nu}_{\max})/\Delta\tilde{\nu})/b]^{2}) \quad (11)$$

Note that with the skewness parameter b = 0 the exponent in eq 11 reduces to a Gaussian. The maximum of eq 11 in the wavelength domain is given by the numerical solution of the nonlinear equation  $(d/d\bar{\nu})\epsilon(\bar{\nu}) = 0$ . The fwhm is given by  $\Delta\bar{\nu}_{1/2} = \Delta\bar{\nu}(\sinh b)/b$ .

**2.2.5.** Solvatochromic Shift Analysis. Assuming that the interaction of the emissive state with the medium can be described as that of a point dipole (magnitude  $\mu$ ) occupying a cavity of radius  $\rho$  in a dielectric continuum, and neglecting the dipole moment of the ground state the energy difference between the emissive state and the ground state  $hc\bar{\nu}_{max}$  is a function of the solvent polarity parameter  $\Delta f$  according to the well-known Lippert-Mataga equation<sup>2,42-46</sup>

$$hc\bar{\nu}_{max} = hc\bar{\nu}_{max}(0) - (2\mu^2/\rho^3)\Delta f \qquad (12)$$

where  $hc\bar{\nu}_{max}(0)$  is the energy difference between the emissive state and the ground state in the gas phase and  $\Delta f$  is defined by the solvent dielectric constant ( $\epsilon$ ) and refractive index (*n*):

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1}$$
(13)

The cylindrical cavity approach<sup>32</sup> was used to estimate the effective radius  $\rho$ .

2.2.6. Multiplicative Bias. There are several sources of systematic error connected with the time-gated optical multichannel analyzer, which have a detrimental influence on the quality of the overall fit. On the one hand, concentration fluctuations are caused by small shot-to-shot variations of the pulse power and of the time delay between the laser pulse and gate pulse (time jitter). Experience shows that the shot-to-shot intensity variations of the excimer laser are well within 10% and that under normal conditions the time jitter is less than 2 ns. In any case, the accuracy of the experiment should benefit from a fairly large number of laser shots used (typically several hundreds), provided there is no drift of laser intensity or timing, a condition normally satisfied by the equipment. The concentration fluctuations cause systematic error in fitting with a kinetic model. On the other hand, the spectral response of the OMA system is not flat and causes systematic error in fitting with a spectral model.

Both types of systematic errors are proportional to the signal, and thus multiplicative. They can to a large extent be corrected by estimation of a multiplicative bias  $\beta$ , which is a function of time in the case of the kinetic model fit, and which is a function of wavelength in the case of the spectral model fit. We will derive the estimation of the bias  $\beta$  for the spectral model fit; the case of the kinetic model fit is treated analogously. In the derivation we will neglect the random error and concentrate on the estimation of the  $n_{\lambda}$  vector  $\beta$ . We have

$$\Psi = \tilde{\Psi} \operatorname{diag}(\beta) \tag{14}$$

where  $\bar{\Psi}$  represents the ideal time-resolved spectrum without systematic error in the wavelength domain. At each wavelength  $\lambda_j$  a column of  $\bar{\Psi}$  is thus multiplied by an unknown multiplicative factor  $\beta_{\lambda_j}$ . Now if we replace  $\tilde{\Psi}$  by the estimated spectral model function  $\hat{\Psi} = \hat{C} \mathbf{E}^{\mathrm{T}}(\hat{\theta})$ , we find for the residuals Z:

$$\mathbf{Z} = \boldsymbol{\Psi} - \hat{\boldsymbol{\Psi}} = \hat{\boldsymbol{\Psi}}(\operatorname{diag}(\beta) - I)$$
(15)

Thus, for each wavelength  $\lambda_j$  we estimate  $\beta_{\lambda_j}$  from a linear regression between a column of  $\hat{\Psi}$  and a column of the residuals Z. When the estimate  $\beta_{\lambda_j}$  differs significantly from 1, we conclude that it represents multiplicative bias. Now in a second fit we can use the estimated multiplicative bias  $\beta$  in the improved spectral model function  $CE^{T}(\theta)$  diag( $\hat{\beta}$ ). Note that this procedure can

TABLE 2: Reduction and Oxidation Potentials (V,  $\pm 0.02$ ) Relative to SCE in DMF As Measured by Cyclic Voltammetry and Singlet Energy  $E_{00}$  (eV)

8 8 **	<u>`</u>			
	$E_{\rm red}(A)$	$E_{ox}(D)$	$E_{ox}(D) - E_{red}(A)$	$E_{00}{}^{a}$
naphthalene	-2.58	-		3.95
1-methylnaphthalene	-2.58 <sup>b</sup>			3.914
1-cyanonaphthalene	-1.90			3.884
1-cyano-4-methyl- naphthalene	-1.91			3.88
1-cyano-4-(cyanomethyl)- naphthalene	-1.72 <sup>e</sup>			3.88
N.N-diethylaniline		0.79		3.904
N,N-diethyl-4- methoxyaniline		0.61		3.65
WS1	-1.87	0.84	2.71	
WS2	-1.88	0.86	2.74	
WS3	-1.68	0.98	2.66	
SS1	-1.86	0.63	2.49	
SS2	-1.87	0.68	2.55	
SS3	-1.68	0.78	2.46	

<sup>a</sup> Singlet energy ( $E_{00}$ ) in cyclohexane solution.  $E_{00}$  represents the mirror point frequency (eV) of absorption and fluorescence. <sup>b</sup> In ACN, from ref 54. <sup>c</sup> From ref 55. <sup>d</sup> From ref 56. <sup>e</sup> Shows an irreversible reduction wave. The first cathodic potential plus 50 mV is taken (scan speed 100 mV/s).<sup>32 f</sup> Shows an irreversible oxidation wave. In analogy to the other compounds  $E_{1/2}$  is taken as the first anodic peak potential minus 50 mV (scan speed 100 mV/s).<sup>32 g</sup> From ref 57.

correct for sharp features in the spectral response of the detection system, not for a smooth change in sensitivity with wavelength because the latter can be "absorbed" into the spectral parameters. When in a certain wavelength range the response is due to one component, e.g., the local fluorescence, this procedure also corrects for systematic deviations of its spectrum from the assumed model function (eq 11).

**2.2.7. Quantum Yields.** From the model fit of the OMA data we find  $\hat{\psi}_{t_l\lambda_j} = \sum_{l=1}^{n_{\text{comp}}} \hat{c}_{lt_l} \hat{\epsilon}_{l\lambda_j}$ . The integral of the  $\hat{c}_{lt_l} \hat{\epsilon}_{l\lambda_j}$  over time and wavelength represents the contribution of component l to the total quantum yield  $\Phi$ .

## 3. Results and Discussion

3.1. Analysis of the Individual Components. From the electrochemical data compiled in Table 2, and as judged by the  $E_{ox}(D) - E_{red}(A)$  values, it can be concluded that in the series of D-bridge-A molecules studied here the energy required for charge separation varies over a 0.85-eV range (i.e., at constant D-A distance) in response to the introduction of substituents. Taking the dialkylaniline-naphthalene D-A pair present in WW1 and WW2 as a basis  $(E_{ox}(D) - E_{red}(A) = 0.79 + 2.58 = 3.37 V)$ , introduction of a cyano group in the acceptor alone (WS1, WS2) leads to a stabilization of D<sup>+</sup>A<sup>-</sup> by 0.65  $\pm$  0.02 eV ( $E_{ox}(D)$  –  $E_{\rm red}(A) = 2.72 \pm 0.02 \, \rm V$ ). Additional introduction of a methoxy group in the donor (SS1 and SS2) enhances the overall stabilizing effect to  $0.85 \pm 0.02 \text{ eV} (E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) = 2.52 \pm 0.03 \text{ V})$ . The electron-releasing 4-methoxy group on the aniline moiety effectively increases the electron donor strength (as measured by  $E_{ox}$ -(D)) by 0.18 V, which corresponds well with the literature data.<sup>47</sup> The overall effect of an additional cyano group on the bridge (i.e., WS3 and SS3) is rather minor. Interestingly though both  $E_{\rm red}(A)$  and  $E_{\rm ox}(D)$  are affected significantly but in an opposite sense. Because this additional cyano group is not conjugatively connected to either the D or A  $\pi$ -system, its effect must be attributed to a combination of inductive and field effects, the latter being related to interaction between the dipole of the cyano group and the charge developed upon reduction of A to A<sup>-</sup> and oxidation of D to  $D^+$ . Such interaction would be expected to be stabilizing in the former and destabilizing in the latter case as indeed borne out by the experimental electrochemical data. Although the various substituents have a rather large influence on the energy of the charge-separated state, their influence on

TABLE 3: Fluorescence of Reference Compounds in Cyclohexane: Spectral Parameters Position  $\bar{\nu}_{max}$  and Width  $\Delta \bar{\nu}$  (10<sup>3</sup> cm<sup>-1</sup>), Skewness *b* (See Eq 11), and Decay Rate Constant *k* (10<sup>9</sup> s<sup>-1</sup>)

	ν̄ <sub>max</sub>	$\Delta \tilde{\nu}$	Ь	k
naphthalene	29.81	3.08	-0.40	0.0114
1-cyanonaphthalene				0.0589
1-cyano-4-methylnaphthalene	29.467	3.091	-0.431	0.0620
1-cyano-4-(cyanomethyl)- naphthalene	29.452	3.023	-0.421	0.0535
N,N-diethylaniline	29.9	3.62	-0.38	0.379
N,N-dimethyl-4-methoxyaniline	27.624	3.338	-0.327	0.350
N,N-diethyl-4-methoxyaniline	27.470	3.244	-0.350	0.356

the energies  $(E_{00})$  of the lowest locally excited state of the chromophores is quite minor (last column of Table 2).

The fluorescence properties of reference compounds in cyclohexane are compiled in Table 3. The spectrum of the acceptor naphthalene (and of its derivatives) showed some vibrational fine structure. The addition of methyl and cyano groups causes only a tiny red shift of about 0.04 eV ( $0.35 \times 10^3$  cm<sup>-1</sup>), but enlarges the decay rate by a factor of 5. The spectrum of the aniline donor is red shifted by as much as 0.30 eV ( $2.43 \times 10^3$  cm<sup>-1</sup>) by the addition of a methoxy group.

Total fluorescence quantum yields are shown in Table 4. In general, flexibly bridged systems (in particular WS1) fluoresce more strongly than semirigidly bridged systems. From the time-integrated emission spectra<sup>26</sup> it appears that, except for WW2 and SW2 in nonpolar media, the local fluorescence of either the D or A chromophore is strongly quenched. Instead more or less bathochromically shifted emission occurs (presumably from a charge-separated state). Especially for the semirigidly bridged systems with a strong acceptor in nonpolar media, this emission displays a band shape indicating the presence of two or more emitting species. It is impossible to estimate the band shapes of these highly overlapping emissions from a single time-integrated emission spectrum. Time-resolved data enable the separation of these emissions when they show different kinetics (see below).

Were it not for the systematic errors we would directly fit a spectrotemporal model (eq 7) to the OMA time-resolved fluorescence data. As described in the section Multiplicative Bias the most natural way to analyze the OMA data, which are collected per spectrum, is the spectral model. First, the SVD of the data is calculated, and the number of components  $n_{\text{comp}}$  is taken equal to the number of singular values and vectors significantly different from noise. Second, a spectral fit with  $n_{\rm comp}$  components according to eq 11 is applied, the multiplicative bias  $\beta(\lambda)$  is estimated (eq 15), and with this  $\hat{\beta}(\lambda)$  a refined fit is performed. Now the spectral parameters have been extracted, and the resulting (linear) concentration parameters (matrix C) are taken as data for a successive kinetic fit. On the other hand, the traces which were collected with better time resolution at up to 12 wavelengths were globally analyzed using a kinetic model with  $n_{\rm comp}$  exponential decays. The resulting decay associated spectra<sup>37</sup> were compared with the OMA results.

**3.1.1. Weak Donor-Strong Acceptor Systems.** We will first consider the WS molecules, some of which were also studied in refs 25, 26, 48, and 49. The results of the decomposition of the OMA data of WS2 in cyclohexane using the spectral model are shown in Figure 1. From the singular value decomposition we find three pairs of singular vectors (not shown) and three singular values (Figure 1c) significantly different from noise.

Apart from some fast decaying local fluorescence around 340 nm (plus signs), which is ascribed mainly to the acceptor, we note two overlapping spectra with  $\bar{\nu}_{max}$  of 26.15 (squares) and 22.96  $\times 10^3$  cm<sup>-1</sup> (circles). The shapes of the accompanying concentration profiles (Figure 1a) could well be fitted with a kinetic model  $M \rightarrow S$ , where M and S are the medium and slow decay rate constants, and the arrow indicates that the slow-decaying, redmost component (circles) is formed from the medium-decaying

TA	BLE	4:	Total	Fluorescence (	Quantum	Yields	₫
----	-----	----	-------	----------------	---------	--------	---

solvent	$\Delta f$	WS1	WS2	WS3	SS1	SS2	SS3	<b>WW</b> 1	WW2	SW1	SW2
n-hexane	0.092	0.24	0.07	0.18	0.04	0.04	0.03	0.16	0.09	0.09	0.10
cyclohexane	0.100	0.50	0.09	0.22	0.07	0.05	0.04	0.24	0.11	0.13	0.12
trans-decalin	0.110	0.70	0.09	0.22	0.09	0.05	0.04	0.31	0.12	0.19	
di-n-hexyl ether	0.170	0.34	0.04	0.03	0.05	0.01	0.03	0.31	0.11	0.15	0.12
di-n-pentyl ether	0.171	0.28	0.03	0.02	0.05	0.01	0.01	0.31	0.11	0.12	0.11
di-n-butyl ether	0.194	0.21	0.02	0.02	0.04	0.01	0.01	0.26	0.10	0.10	0.10
di-n-propyl ether	0.213	0.18	0.02	0.02	0.03	0.01	0.01	0.22	0.10	0.08	0.07
diisopropyl ether	0.237	0.14	0.01	0.01	0.02	0.01	0.01	0.20	0.07	0.07	0.04
diethyl ether	0.251	0.12	0.01	0.01	0.01	<0.01	<0.01	0.18	0.04	0.07	0.01
n-butyl acetate	0.267	0.09	0.01	0.01	<0.01	<0.01	<0.01	0.16	0.02	0.07	0.01
ethyl acetate	0.292	0.06	0.01	0.01	<0.01	<0.01	<0.01	0.10	0.01	0.06	0.01
tetrahydrofuran	0.308	0.08	0.01	0.01	<0.01	<0.01	<0.01	0.07	0.01	0.05	0.01
dichloromethane	0.319	0.09	0.01	0.01		<0.01	<0.01	0.05	0.01	0.04	0.01
ethanol	0.379	<0.01	<0.01					0.04	0.01	<0.01	0.01
acetonitrile	0.393	<0.01	<0.01					0.05	0.01	<0.01	<0.01



Figure 1. Decomposition of the OMA data of WS2 in cyclohexane using the spectral model: squares, ECT; circles, CCT; plus signs, local fluorescence. (c) Logarithm of the first 10 singular values as calculated from SVD of the data. Regarding the scaling in (a) and (b), since the product  $c\epsilon^{T}$  is estimated, we calculate the extremum of this product per component, and scale according to the maximum of the extrema of all components. Here we have  $\max(c_1\epsilon_1^T) = (0.7)^2 \max(c_2\epsilon_2^T)$ . The curves are thus scaled according to their contribution to  $\Psi$ .



Figure 2. Decomposition of the trace data of WS2 in cyclohexane using the kinetic model: squares,  $k_1 = 0.13 \times 10^9 \text{ s}^{-1}$ , decay rate of ECT; circles,  $k_2 = 0.09 \times 10^9 \text{ s}^{-1}$ , decay rate of CCT; plus signs,  $k_3 = 1.6 \times 10^9 \text{ s}^{-1}$ , decay rate of local fluorescence. The solid line in (a) is the system response. (b) Decay associated spectra. (c) Logarithm of the first 10 singular values as calculated from SVD of the trace data. No rescaling is done, so the amplitudes of the DAS represent the number of excited states at time zero after a hypothetical  $\delta$ -pulse input.

component (squares). We have previously interpreted this as evidence for harpooning<sup>25</sup> in which the blue emission (squares) stems from a primarily formed extended CT (ECT) state from which a folded contact CT (CCT) state emitting at longer wavelengths (circles) is formed. The trace data again show three significant singular values (Figure 2c) and can be fitted with three decays (Figure 2a); Figure 2b shows the DAS. Clearly the spectrum belonging to the rate constant  $k_1 = 0.13 \times 10^9 \text{ s}^{-1}$ (squares) possesses negative amplitudes at wavelengths greater than 400 nm. As demonstrated in eq 10, these negative amplitudes are due to the formation of the slow-decaying redmost component from the medium-decaying component. By applying a kinetic model  $M \rightarrow S$ , we find spectra with shapes like in Figure 1b with  $\bar{\nu}_{\rm max}$  of 26.0 and 22.9  $\times$  10<sup>3</sup> cm<sup>-1</sup>. Given the limited spectral resolution of the trace data, we consider this an excellent agreement. WS2 displays a similar behavior in all saturated hydrocarbon solvents (from 2-methylbutane up to cis-decalin). In solvents of higher polarity no evidence for harpooning is found. In those polar solvents  $(0.17 \le \Delta f \le 0.308)$  where WS2 shows charge-transfer fluorescence with sufficient intensity for analysis a single CT emission is found. To relate the spectral parameters of the different CT emissions found in the range of solvents, we

plotted  $\bar{\nu}_{max}$  and  $\Delta \bar{\nu}_{1/2}$  as a function of the solvent polarity  $\Delta f$  in Figure 3c,d. The circles in Figure 3c represent the CCT state whereas the squares indicate the ECT state. The squares could well be fitted by a straight line with a negative slope, the parameters of which can be interpreted using the Lippert-Mataga equation (12). Thus, we estimate a dipole moment of 28 D (Table 7) which corresponds to an effective charge separation of 6 Å, compatible with the extended structure of WS2 in the ground state being retained in the ECT state. The straight line fit of the circles possesses a small positive slope. We hypothesize that in nonpolar saturated hydrocarbon solvents the D+A- distance of the folded CCT state of WS2 increases with increasing dielectric constant because the Coulombic attraction forcing D<sup>+</sup> and A<sup>-</sup> together is diminished. Therefore less electrostatic energy is gained, giving rise to an increasing  $hc\bar{\nu}_{max}(0)$ . The fwhm of the spectra,  $\Delta \bar{\nu}_{1/2}$ , displays only a small variation, with values between 4.4 and  $5.2 \times 10^3$  cm<sup>-1</sup> for both the ECT and the CCT emissions (indicated by squares and circles in Figure 3d).

The behavior of WS3 is similar to that of WS2; compare parts e and c of Figure 3. Supplementary evidence for the existence of the two CT emissions comes from steady-state spectra measured at different temperatures. Using a two-component spectral model (admittedly the temperature independence of spectral shape in



Figure 3. Solvent polarity  $\Delta f$  versus the spectral-shape parameters  $\bar{\nu}_{max}$  and  $\Delta \bar{\nu}_{1/2}$  of WS1 (a, b), WS2 (c, d) and WS3 (e, f): squares, ECT; circles, CCT; triangles, second CCT. Filled symbols have been derived from steady-state spectra at different temperatures.

a solvent has its limitations), we find a satisfactory decomposition. The spectral parameters of these fits are included in Figure 3e,f (filled symbols). The agreement in  $\bar{\nu}_{max}$  is satisfactory, whereas the  $\Delta \bar{\nu}_{1/2}$  agrees for the red CT emission but is considerably smaller for the blue CT emission (compare open and filled squares in Figure 3f). Apparently the estimation of the red tail of the ECT emission which overlaps with the CCT emission (e.g., Figure 1b) is difficult. The additional cyano group of WS3 causes several changes with respect to WS2; compare parts c and d to parts e and f of Figure 3. Firstly, the intercept of the ECT line (squares in Figure 3e) is lowered by  $1.4 \times 10^3$  cm<sup>-1</sup> (=0.17 eV) (Table 7). Secondly, the CCT line (circles in Figure 3e) now shows a



Figure 4. Decomposition of the trace data of WS1 in *n*-hexane using the kinetic model: squares,  $k_1 = 1 \times 10^9 \text{ s}^{-1}$ , decay rate of ECT; circles,  $k_2 = 0.0238 \times 10^9 \text{ s}^{-1}$ , decay rate of major CCT; triangles,  $k_3 = 0.08 \times 10^9 \text{ s}^{-1}$ , decay rate of minor CCT.

TABLE 5: Decay Rate Constants  $(10^9 \text{ s}^{-1})$  of CT Emissions (ECT = Extended CT State, CCT = Contact CT State) from Flexibly Bridged Systems in Nonpolar and Intermediately Polar Solvents

			WS1		S	S1	W	W1	SV	<b>V</b> 1
solvent	$\Delta f$	ECT	CCT1	CCT2	CCT1	CCT2	CCT1	CCT2	CCT1	CCT2
2-methylbutane	0.091	0.9	0.0133	0.032						
n-hexane	0.092	1.0	0.0238	0.08	0.028	0.8	0.052	0.16	0.0395	0.080
n-nonane	0.098	0.8	0.0145	0.032						
cyclohexane	0.100	1.1	0.0156	0.06	0.027	>1	0.043	0.18	0.0347	0.099
methylcyclohexane	0.100	0.7	0.0176	0.05						
n-tetradecane	0.102	0.7	0.0127	0.030						
n-hexadecane	0.103	0.7	0.0130	0.029						
trans-decalin	0.110	1.0	0.0145	0.06	0.027	1	0.037	0.15	0.0305	0.091
cis-decalin	0.111	0.6	0.0140	0.036						
di-n-hexyl ether	0.170	1.0	0.0176	0.11	0.084		0.030	0.13	0.033	0.12
di-n-pentyl ether	0.171	1.3	0.0179	0.10	0.045		0.030	0.13	0.032	0.074
di-n-butyl ether	0.194	0.9	0.0212	0.10	0.060		0.039	0.35	0.040	0.11
di-n-propyl ether	0.213		0.0277		0.078		0.040	0.37	0.049	
diisopropyl ether	0.237		0.0330		0.089		0.050	0.84	0.033	0.14

small negative slope, and the CCT width (Figure 3f) is about 0.7  $\times 10^3$  cm<sup>-1</sup> smaller. Regarding the kinetics, in particular the CCT state possesses a rate constant about half as large as in WS2 (open versus filled circles in Figure 8b; see also Tables 9S and 10S in the supplementary material). This explains to a great extent the 2 times higher quantum yields found with apolar solvents (columns three and four of Table 4).

We now focus our attention on the flexibility bridged WS1. The trace data of WS1 in n-hexane reveal three significant singular values (Figure 4c) and can be fitted with three decays (Figure 4a), with the DAS (Figure 4b) of the fastest rate constant (squares) possessing negative amplitudes at wavelengths greater than 400 nm, analogous to Figure 2b. Thus, these data can be fitted with a model which incorporates the formation of the slow-decaying component (circles) from the fast-decaying component. Thus, in the flexibly bridged WS1 we again find evidence for harpooning, but with a rate constant about 5 times larger than in the semirigidly bridged WS2 (compare Table 5, column three, and the filled squares in Figure 8a; see also Tables 8S and 9S in the supplementary material). Next to these two dominant components a third, intermediate decay is found (triangles in Figure 4a,b), with a spectrum somewhat more blue than that of the CCT which is formed from the ECT. It may originate from a differently folded CCT. It cannot be concluded whether this component also grows in from the ECT. The OMA data lack the time resolution necessary to demonstrate harpooning. However, they also indicate the presence of more than one CCT conformer. We first estimate the spectral shape of the longest living component from the latest spectra, and kept its parameters fixed in the successive fit using the full data set. In this way a reliable decomposition of these highly overlapping spectra was possible (Figure 5). The blue emission indicated by the squares is attributed to the ECT species, whereas the most blue emission indicated by the plus signs is attributed to local fluorescence and Raman scattering of the solvent. The estimated spectral parameters of the ECT emission display more scatter (squares in Figure 3a,b) due to overlap with the neighboring emissions (Figure 5b). The  $\bar{\nu}_{max}$  is about 10<sup>3</sup> cm<sup>-1</sup> higher than the value found with WS2. We established harpooning in trace data of WS1 in all

solvents less polar than di-n-butyl ether (Table 5). The second CCT conformer (with the higher  $\bar{\nu}_{max}$  and the faster decay) was found in both trace and OMA data in these solvents also. Compelling evidence for the existence of an emissive ECT species in WS1 comes from steady-state spectra measured at different temperatures.<sup>26</sup> Using a three-component spectral model, we find a satisfactory decomposition shown in Figure 6. At temperatures below 230 K (the melting point of trans-decalin in 243 K) a blue emission contributes substantially. However, the red emission is still present at 144 K. The blue ECT emission possesses a  $\bar{\nu}_{max}$  of 26.9  $\times$  10<sup>3</sup> cm<sup>-1</sup>, which is comparable to the values found with the OMA data (compare open and filled squares in Figure 3a). Due to the large overlap of the two CCT spectra a reliable decomposition of the red CT emission (circles in Figure 6) was impossible. Note that there is only a little bit of local fluorescence around 330 nm as indicated by the plus signs in Figure 6a. The SVD (Figure 6c) indicates more than three significant singular values, the interpretation of which is further complicated by temperature effects upon the spectral shapes. Further temperature studies are in progress.

In solvents more polar than diisopropyl ether only the ECT conformer is present as indicated by the squares in the  $\Delta f \bar{\nu}_{max}$ plot (Figure 3a). The negative slope of the fit to the squares was similar to the slope found with WS2 which confirms that the CT fluorescence stems from an ECT (Table 7). In nonpolar saturated hydrocarbon solvents only a very small negative slope is found with the CCT emissions (circles and triangles in Figure 3a). The width of the dominant CCT (circles in Figure 3b) is clearly smaller than with WS2 (and somewhat smaller than with WS3). The ECT width in nonpolar media is comparable to the CCT width (squares and circles in left part of Figure 3b; see also Table 8S). In polar solvents it is somewhat smaller than with WS2. The decay rates of the dominant CCT conformer are even smaller than with WS3 (compare column four of Table 5 with the circles in Figure 8b), explaining in part the very high quantum yields of WS1 (Table 4, column three).

**3.1.2. Strong Donor-Strong Acceptor Systems.** Next we turn to the SS systems. In general, they behave similar to their WS counterparts. The additional methoxy group lowers the  $\bar{\nu}_{max}$  of

860 The Journal of Physical Chemistry, Vol. 98, No. 3, 1994



Figure 5. Decomposition of the OMA data of WS1 in *n*-hexane using the spectral model: squares, ECT; circles, major CCT; triangles, minor CCT; plus signs, local fluorescence.



Figure 6. Decomposition of steady-state spectra of WS1 in *trans*-decalin at different temperatures using the spectral model: squares, ECT; circles, CCT; plus signs, local fluorescence.

the CT fluorescence by  $2.7 \times 10^3$  cm<sup>-2</sup> (=0.33 eV) (Table 7 and Tables 8S-13S in the supplementary material), which is to be compared with the 0.18-V lowering in donor oxidation potential found with the reference compounds (Table 2). The slopes of the lines in the  $\Delta f - \bar{\nu}_{max}$  plots in Figure 7a,c,e are in general comparable to those of the WS counterparts (Figure 3a,c,e) (Table 7). However, in contrast to WS2, the CCT line of SS2 (circles in Figure 7c) shows only a very small (if any) positive slope, whereas SS3 (only three circles in Figure 7e) shows a more negative slope than WS3. The half-widths  $\Delta \bar{\nu}_{1/2}$  are considerably smaller in SS2 than in WS2 (compare Figure 7d with Figure 3d) in nonpolar solvents, whereas a positive slope is somewhat more clearly present in more polar solvents. In trace data of SS1 in apolar solvents no clear evidence for harpooning could be found, in contrast to WS1. This is most probably due to insufficient time resolution (0.2-ns channel width, 7-ns fwhm system response), since at 400 nm the estimated lifetime (reciprocal of the rate constant) is smaller than one channel width (0.2 ns). In fact, at somewhat lower temperatures clear evidence for harpooning was found in methylcyclohexane (Scherer and Van Stokkum, unpublished observations). Some evidence for a second CCT was found, with a  $\bar{\nu}_{max}$  about 10<sup>3</sup> cm<sup>-1</sup> higher. Fitting the blue ECT emission from OMA data was even harder than with WS1; therefore, some half-widths  $\Delta \bar{\nu}_{1/2}$  are lacking in Figure 7b. Note that the kinetics of SS1 are about twice as fast as in WS1 (Table 5), which partly explains the much lower quantum yields (Table 4).

We now discuss some properties of CT emissions in polar solvents. Both SS1 and WS1 show a weak, very fast decaying ECT fluorescence when  $\bar{\nu}_{max} < 17 \times 10^3 \text{ cm}^{-1}$  (Table 6 and also Tables 8S and 11S in the supplementary material). With WS2 and WS3 no  $\bar{\nu}_{max}$  lower than  $16.7 \times 10^3$  cm<sup>-1</sup> was found. With SS2 the minimal  $\bar{\nu}_{max}$  is  $15.9 \times 10^3$  cm<sup>-1</sup>, whereas with SS3 two  $\bar{\nu}_{\rm max} < 15 \times 10^3 \, {\rm cm}^{-1}$  were found, both weak, very fast decaying ECT fluorescence (Table 13S). In Table 6 we compiled the decay rates of ECT emissions in polar solvents. Compared to Table 4 we note that in general faster decay rates correlate with smaller total fluorescence quantum yields  $\Phi$ . In Figure 8a we have plotted the ECT decay rates of the semirigidly bridged harpooning systems WS2, WS3, SS2, and SS3 in nonpolar solvents as a function of the solvent viscosity. There is a clear downward trend going toward more viscous solvents, which can be related to the conformational change involved in the harpooning. The CCT decay rates (Figure 8b) lack a clear trend. The steeper declines of SS3 are based upon three points only (plussed squares in Figure 8a, plussed circles in Figure 8b). More elaborate studies concerning viscosity effects upon harpooning are under way.

3.1.3. Weak Donor-Weak Acceptor Systems. Finally, we discuss the systems possessing a weak, naphthalene acceptor. With flexibly or semirigidly bridged molecules ECT fluorescence is not found in saturated hydrocarbon solvents, simply because the energy of the extended CT state is greater than that of the locally excited state (case I; see also ref 26). In these solvents the flexibly bridged systems display CCT fluorescence (circles and triangles in Figures 10a and 13a). ECT emission is only detected in solvents more polar than di-n-propyl ether (squares in Figures 10a,c and 13a,c). The local fluorescence in the semirigidly bridged WW2 shows two components in solvents up to diisopropyl ether; in more polar solvents it could no longer be reliably decomposed. An example, WW2 in trans-decalin, is shown in Figure 9. The crossed triangles represent the scattered 308-nm laser light broadened by the bandwidth of the spectrograph. Part of the longer lasting fluorescence (asterisks) seems to grow in from the fast-decaying emission (diamonds); compare with Figure 1a. A kinetic fit of the concentration profiles (Figure 9a) established that the concentration indicated by the asterisks consisted of a fast decay with a negative amplitude which was about half as large as the amplitude of the slow decay. At first glance these two components are ascribed to, respectively, the naphthalene and the N.Ndiethylaniline chromophores, since compared to the parameters of the reference compounds in Table 3 we note a reasonable agreement between the long-lasting emission,  $k = 0.09 \times 10^9 \text{ s}^{-1}$ . in cyclohexane and the decay rates of the substituted naphthalenes. whereas the  $\bar{\nu}_{max} \approx 29 \times 10^3$  cm<sup>-1</sup> is somewhat smaller. The fast decay rate of about  $0.4 \times 10^9$  s<sup>-1</sup> agrees well with the decay rate of N,N-diethylaniline, but the  $\bar{\nu}_{\rm max} \approx 27.6 \times 10^3 \ {\rm cm^{-1}}$  is considerably smaller. If we assume that both chromophores are excited and energy transfer occurs between them, we expect DAS which are linear combinations of the real spectra.<sup>50</sup> The same holds with the spectral model: the spectrum of the longer lasting fluorescence is a weighted sum (with positive coefficients) of the highly overlapping spectra of the two chromophores. On the other hand, the fast-decaying emission can correspond to a weighted sum (with possibly a negative coefficient, analogous to eq 10) of the real spectra. Thus, we hypothesize that such a negative coefficient is present with the emission indicated by the diamonds in Figure 9a, which leads to the unexpectedly small  $\bar{\nu}_{max}$ . In four out of eight solvents the kinetics showed indications for energy transfer. The spectral overlap between the two



Figure 7. Solvent polarity  $\Delta f$  versus the spectral-shape parameters  $\bar{\nu}_{max}$  and  $\Delta \bar{\nu}_{1/2}$  of SS1 (a, b), SS2 (c, d), and SS3 (e, f): squares, ECT; circles, CCT; triangles, second CCT.

emissions increased with increasing solvent polarity. The ECT emission displayed the expected behavior (Figure 10c, squares).

The flexible counterpart of WW2, WW1, resembles WS1, apart from the ECT emission in nonpolar solvents. The OMA data of WW1 in *n*-hexane can again be fitted with three components (Figure 11; compare to Figure 5). Two of these are

ascribed to folded CT states, whereas the blue component is ascribed to local fluorescence. Supplementary evidence comes again from steady-state spectra measured at different temperatures. In this case lowering the temperature results in the growth of an emission at 330 nm, the location of the local emission (Figure 6 of ref 26). The contribution of the second CCT is larger in

TABLE 6: Decay Rate Constants (10<sup>9</sup> s<sup>-1</sup>) of the Extended CT State (ECT) in Polar Solvents



Figure 8. Decay rates of semirigidly bridged WS and SS systems which show harpooning in nonpolar solvents as a function of the solvent viscosity  $\eta$ : (a) ECT; (b) CCT; filled symbols, WS2; open symbols, WS3; crossed symbols, SS2; plussed symbols, SS3.



Figure 9. Decomposition of the OMA data of WW2 in *n*-hexane using the spectral model: crossed triangles, scattered laser pulse; diamonds and asterisks, local emission; see text.

WW1 than in WS1 (Table 14S in the supplementary material). The trace data (Figure 12) now show no negative amplitudes and thus no evidence of ingrow (compare to Figure 4). Thus, following ref 26, we hypothesize that folding precedes charge transfer in WW1 in nonpolar solvents. This is analogous to the D-(CH<sub>2</sub>)<sub>3</sub>-A systems studied by Mataga and co-workers<sup>8,10,11</sup> which were already mentioned in the Introduction. In time-resolved fluorescence studies evidence for a conformational change preceding charge transfer was found. In the nonpolar solvents hexane and decalin the exciplex emission possessed a rise time constant of, respectively, 4 and 8 ns. The  $\Delta f - \bar{\nu}_{max}$  plot (Figure 10a) resembles that of WS1 (Figure 3a), the difference in acceptor strength causing an upward shift of  $\bar{\nu}_{max}$  of the CCT lines of 2.5 × 10<sup>3</sup> cm<sup>-1</sup> (=0.31 eV), which is less than the  $E_{ox}(D) - E_{red}(A)$  difference of 0.6 V.

3.1.4. Strong Donor-Weak Acceptor Systems. The strong donor counterpart of WW2, SW2, also displays ECT fluorescence starting with di-*n*-propyl ether, but now only until dichloromethane (compare squares in Figures 10c and 13c). The local fluorescence consisted only of a fast-decaying component, with a spectrum resembling that of the donor chromophore which has the lowest excitation energy (cf. Table 2). In cyclohexane the methoxyaniline local fluorescence of SW2 and SW1 possesses a  $\bar{\nu}_{max}$  of,

respectively, 27.1 and  $27.0 \times 10^3$  cm<sup>-1</sup> which is similar to the 27.5  $\times$  10<sup>3</sup> cm<sup>-1</sup> of the reference compound N,N-diethyl-4-methoxyaniline (Table 3). The spectral shape agrees well with the reference compound in SW2, whereas the scatter and greater width in SW1 are due to the overlap with the CT emissions. In polar solvents, where the overlap becomes small, the widths are comparable (compare diamonds in Figure 13b.d). The flexible counterpart of SW2, SW1, resembles SS1, but again as for WW1 lacks ECT emission in nonpolar solvents. The difference in intercepts of the lower CCT lines for SW1 and SS1 amounts to  $3.3 \times 10^3$  cm<sup>-1</sup> (=0.41 eV), which is again less than the  $E_{ox}(D)$  $-E_{red}(A)$  difference of 0.6 V. In traces of SW1 in nonpolar solvents a second CCT was clearly present, comparable to WW1. Again no evidence for harpooning was found. At about the polarity of diisopropyl ether the transition from the CCT to the ECT species takes place.

3.2. Comparison of the Semirigid Piperidine-Bridged Systems. The systems WS2, WS3, SS2, and SS3 are all equipped with a very strong electron acceptor, and their emissive behavior in nonpolar solvents can be characterized by a case III situation in contrast to the WW2 and SW2 systems which typically are described by case I. Analysis of the fluorescent behavior of the harpooning systems shows that the blue CT emission in these



Figure 10. Solvent polarity  $\Delta f$  versus the spectral-shape parameters  $\bar{\nu}_{max}$  and  $\Delta \bar{\nu}_{1/2}$  of WW1 (a, b) and WW2 (c, d): squares, ECT; circles, CCT; triangles, second CCT; diamonds and asterisks, local emission; see text.



Figure 11. Decomposition of the OMA data of WW1 in n-hexane using the spectral model: circles, major CCT; triangles, minor CCT; plus signs, local fluorescence.



Figure 12. Decomposition of the trace data of WW1 in *n*-hexane using the kinetic model: circles,  $k_1 = 0.16 \times 10^9 \text{ s}^{-1}$ , decay rate of first CCT; triangles,  $k_2 = 0.052 \times 10^9 \text{ s}^{-1}$ , decay rate of second CCT; plus signs,  $k_3 = 6 \times 10^9 \text{ s}^{-1}$ , decay rate of local fluorescence.

solvents can satisfactorily be fitted with the Lippert-Mataga equation (12). The thus obtained slopes and intercepts are tabulated in Table 7. The differences in intercepts reflect the changes in D-A strength. Comparing WS with SS, it is found that the methoxy group lowers the charge-separated state by about 0.3 eV, which is somewhat more than expected from the



Figure 13. Solvent polarity  $\Delta f$  versus the spectral-shape parameters  $\bar{\nu}_{max}$  and  $\Delta \bar{\nu}_{1/2}$  of SW1 (a, b) and SW2 (c, d): squares, ECT; circles, major CCT; triangles, minor CCT; diamonds, methoxyaniline.

cyclic voltammetry measurements (Table 2). The bridgehead cyano group has a stabilizing effect of 0.16 eV, identical to the difference found in the separate acceptor chromophores. The negative slope values of Table 7 are quite similar ((41-44) × 10<sup>3</sup> cm<sup>-1</sup>), and using  $\rho = 5.7$  Å, dipole moments of 28 D are calculated. The dipole moments found in this study agree well with those found using the time-resolved microwave conductivity technique.<sup>49</sup> These giant dipoles confirm the ECT nature of the emitting species, as these dipoles correspond to effective charge separation distances of 5.8 Å. These calculated distances agree rather well with center to center distances between the nitrogen donor and the center of the acceptor, provided that the piperidine bridge adopts a chair conformation with the aromatic substituents in equatorial positions.

The Lippert–Mataga equation cannot be applied straightforwardly for the red-shifted emission found in nonpolar solvents. This emission, which we attribute to the folded CCT conformation,<sup>25</sup> shows a clear positive slope in WS2, whereas with the other systems the slopes are zero or negative. As the folded CCT species is most likely in a highly strained boat conformation, its precise geometric structure is expected to be more sensitive to the solvent than the CCT conformation of the flexible counterparts.

It should be noted that the slope values of the piperidine systems with the bridgehead cyano group cannot be compared directly to the systems without this group. From studies on cyclohexane derivatives<sup>51</sup> it is known that such a cyano group has a small preference for an equatorial conformation. Although the equatorial preference of the naphthyl unit is much larger, these systems will be slightly destabilized, resulting in a somewhat lower interconversion barrier and CCT species with smaller steric strain.

The difference in band position between the extended CT and folded CT reflects the electrostatic energy gain minus the loss of solvation energy. All four harpooning systems start off with 9–11 kcal/mol in *n*-hexane. But this net gain falls off rapidly, especially for WS2: in 2-methylbutane 10.8 kcal/mol and in *cis*-decalin only 5.3 kcal/mol has remained. In the other systems there is a more gradual decrease in energy.

Assuming a full charge separation the harpooning involves a change in Coulombic energy of  $\Delta E_{\rm C} = (e^2/4\pi\epsilon_0\epsilon_r)(1/r_{\rm CCT} - 1/r_{\rm ECT})$ . Inserting  $r_{\rm ECT} = 5.7$  Å and  $r_{\rm CCT} = 3.5$  Å (vide infra), we find  $\Delta E_{\rm C} = 1.6/\epsilon_r$  eV. Thus, in 2-methylbutane  $\Delta E_{\rm C} = 0.87$  eV, decreasing to 0.73 eV in *cis*-decalin. Taking into account a greater  $r_{\rm CCT}$  in *cis*-decalin would make this difference in  $\Delta E_{\rm C}$  even larger. The difference in  $\bar{\nu}_{\rm max}$  in these solvents (respectively 0.47 and 0.23 eV) thus indicate a loss of solvation energy of, respectively, 0.4 and 0.5 eV. The decrease of the driving force for harpooning with increasing  $\epsilon$  was also discussed in ref 24. This has to be included next to the effect of solvent viscosity upon the harpooning (Figure 8a).

According to case I, WW2 and SW2 lack CT emission in nonpolar solvents. Only local emission is observed in both systems. In SW2 this emission is ascribed to the methoxyaniline donor. In WW2 not only donor fluorescence is observed, but also some resulting from the naphthalene acceptor. This can be understood

TABLE 7: Lippert-Mataga Fit (See Eq 12) of Position  $\bar{\nu}_{max}$  versus Solvent Polarity  $\Delta P$ 

Δf	intercept <sup>b</sup>	-slope <sup>b</sup>	ρ (Å)	μ(D)	$\Delta \bar{\nu}_{1/2}{}^{b,c}$
0.091-0.393	31.3(3) <sup>d</sup>	43(1) <sup>d</sup>	6.0	30	2.9-4.6
0.091-0.237	23.9(2)	12(2)	6.0	16	2.4-3.1
0.091-0.237	22.87(5)	10.0(4)	6.0	15	3.7-3.9
0.091-0.308	30.3(3)	44(2)	5.7	28	4.4-4.9
0.0910.111	19.2(5)	-38(5)	5.7		4.6-5.2
0.091-0.308	28.9(3)	42(2)	5.7	28	4.4-4.9
0.091-0.111	21.6(2)	2(2)	5.7	6	4.1
0.092-0.308	27.5(4)	41(2)	6.0	29	4.1-4.4
0.092-0.110	20.3e				2.9e
0.092-0.237	20.3(2)	10. <b>9</b> (7)	6.0	15	3.8-4.1
0.091-0.267	27.4(3)	41(2)	5.7	28	3.8-5.3
0.091-0.110	19.2(3)	-2(3)	5.7	-	4.1-4.4
0.092-0.267	26.1(7)	42(4)	5.7	28	4.3–5.0
0.092-0.110	19.21(5)	6.9(5)	5.7	11	4.0
0.308-0.393	35.0(7)	39(2)	6.0	29	4.3-5.6
0.092-0.251	26.8(2)	9(1)	6.0	14	2.7–3.9
0.092-0.251	25.31(6)	5.3(4)	6.0	11	4.0-4.4
0.213-0.393	33(2)	36(4)	5.7	26	3.4-5.7
0.0920.237	29.87(5)	6.8(3)			4.0-5.3
0.0920.237	27.2(2)	-2(1)			5.2
0.237-0.393	29.0(6)	30(2)	6.0	25	4.0-5.4
0.0920.393	27.5(2)	3.3(7)			3.6-6.8
0.092-0.237	25.0(4)	11(2)	6.0	15	2.6-3.4
0.092-0.237	23.6(2)	7.6(7)	6.0	13	4.0
0.213-0.319	31(3)	38(8)	5.7	26	3.5-7.1
0.0920.393	27.7(3)	5(1)			3.5-3.8
	Δf 0.091-0.393 0.091-0.237 0.091-0.237 0.091-0.308 0.091-0.111 0.091-0.308 0.092-0.308 0.092-0.110 0.092-0.237 0.091-0.267 0.091-0.267 0.092-0.267 0.092-0.267 0.092-0.251 0.092-0.251 0.092-0.237 0.237-0.393 0.092-0.237 0.092-0.237 0.092-0.237 0.092-0.237 0.092-0.237 0.092-0.237 0.092-0.237 0.213-0.319 0.092-0.237	$\begin{array}{c c} \Delta f & \text{intercept}^b \\ \hline 0.091-0.393 & 31.3(3)^d \\ 0.091-0.237 & 23.9(2) \\ 0.091-0.237 & 22.87(5) \\ 0.091-0.308 & 30.3(3) \\ 0.091-0.111 & 19.2(5) \\ 0.091-0.308 & 28.9(3) \\ 0.091-0.111 & 21.6(2) \\ 0.092-0.308 & 27.5(4) \\ 0.092-0.308 & 27.5(4) \\ 0.092-0.110 & 20.3^e \\ 0.092-0.237 & 20.3(2) \\ 0.091-0.267 & 27.4(3) \\ 0.092-0.267 & 26.1(7) \\ 0.092-0.267 & 26.1(7) \\ 0.092-0.251 & 26.8(2) \\ 0.092-0.251 & 26.8(2) \\ 0.092-0.237 & 29.87(5) \\ 0.092-0.237 & 25.0(4) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.6(2) \\ 0.092-0.237 & 25.7(3) \\ \hline \end{array}$	$\begin{array}{c cccc} \Delta f & \text{intercept}^b & -\text{slope}^b \\ \hline 0.091-0.393 & 31.3(3)^d & 43(1)^d \\ 0.091-0.237 & 23.9(2) & 12(2) \\ 0.091-0.237 & 22.87(5) & 10.0(4) \\ 0.091-0.308 & 30.3(3) & 44(2) \\ 0.091-0.111 & 19.2(5) & -38(5) \\ 0.091-0.308 & 28.9(3) & 42(2) \\ 0.091-0.111 & 21.6(2) & 2(2) \\ 0.092-0.308 & 27.5(4) & 41(2) \\ 0.092-0.110 & 20.3^e \\ 0.092-0.237 & 20.3(2) & 10.9(7) \\ 0.091-0.110 & 19.2(3) & -2(3) \\ 0.092-0.267 & 26.1(7) & 42(4) \\ 0.092-0.110 & 19.21(5) & 6.9(5) \\ 0.308-0.393 & 35.0(7) & 39(2) \\ 0.092-0.251 & 26.8(2) & 9(1) \\ 0.092-0.251 & 25.31(6) & 5.3(4) \\ 0.213-0.393 & 33(2) & 36(4) \\ 0.092-0.237 & 27.5(2) & 3.3(7) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.092-0.237 & 25.0(4) & 11(2) \\ 0.213-0.319 & 31(3) & 38(8) \\ 0.092-0.393 & 27.7(3) & 5(1) \\ \end{array}$	$\begin{array}{c cccc} \Delta f & \text{intercept} & -\text{slope}^{b} & \rho (\Bar{A}) \\ \hline 0.091-0.393 & 31.3(3)^{d} & 43(1)^{d} & 6.0 \\ 0.091-0.237 & 23.9(2) & 12(2) & 6.0 \\ 0.091-0.237 & 22.87(5) & 10.0(4) & 6.0 \\ 0.091-0.308 & 30.3(3) & 44(2) & 5.7 \\ 0.091-0.308 & 30.3(3) & 44(2) & 5.7 \\ 0.091-0.111 & 19.2(5) & -38(5) & 5.7 \\ 0.091-0.308 & 28.9(3) & 42(2) & 5.7 \\ 0.092-0.308 & 27.5(4) & 41(2) & 6.0 \\ 0.092-0.110 & 20.3^{e} & 0.092-0.237 & 20.3(2) & 10.9(7) & 6.0 \\ 0.091-0.267 & 27.4(3) & 41(2) & 5.7 \\ 0.092-0.267 & 26.1(7) & 42(4) & 5.7 \\ 0.092-0.267 & 26.1(7) & 42(4) & 5.7 \\ 0.092-0.251 & 26.8(2) & 9(1) & 6.0 \\ 0.213-0.393 & 35.0(7) & 39(2) & 6.0 \\ 0.213-0.393 & 27.5(2) & 3.3(7) & 0.092-0.237 & 29.87(5) & 6.8(3) \\ 0.092-0.237 & 27.2(2) & -2(1) & 0.237-0.393 & 27.5(2) & 3.3(7) \\ 0.092-0.237 & 25.0(4) & 11(2) & 6.0 \\ 0.092-0.237 & 23.6(2) & 7.6(7) & 6.0 \\ 0.092-0.237 & 23.6(2) & 7.6(7) & 6.0 \\ 0.092-0.237 & 23.6(2) & 7.6(7) & 6.0 \\ 0.213-0.319 & 31(3) & 38(8) & 5.7 \\ 0.092-0.393 & 27.7(3) & 5(1) \\ \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

 ${}^{a}\rho$  is the effective radius applied, and  $\mu$  is the excited-state dipole moment calculated. In the last column the variation of the spectral halfwidth  $\Delta \bar{\nu}_{1/2}$  with solvent polarity is given.  ${}^{b}$  In 10<sup>3</sup> cm<sup>-1</sup>.  ${}^{c}$  Disregarding outliers.  ${}^{d}$  The number in parentheses is the standard error in the last digit.  ${}^{e}$  Average of three values from trace experiments.

as upon photoexcitation at 308 nm both chromophores are excited. Due to the higher molecular absorption coefficient, the shortliving aniline donor gets most of the excitation energy, but some may be transferred back and forth to the naphthalene chromophore, as there is large spectral overlap. Experiments with a better time resolution (especially at the blue edge of the naphthalene spectrum) are necessary to establish energy transfer unequivocally. In solvents more polar than di-*n*-propyl ether electron transfer is thermodynamically feasible. This can easily be recognized from the strong solvatochromic behavior of the red-shifted emission. The large distance between D and A imposed by the piperidine spacer results in slope values of  $36 \times 10^3$  and  $38 \times 10^3$  cm<sup>-1</sup> for the dipolar state. The large dipole moments of 26 D indicate once more that the emission found in these polar solvents arises from an ECT species.

3.3. Comparison of the Flexible Trimethylene-Bridged Systems. Examining the emissive behavior of the flexibly bridged D-A systems in a  $\Delta f - \bar{\nu}_{max}$  plot, a dichotomy is present between the systems possessing a weak acceptor (WW1, SW1) or a strong acceptor (WS1, SS1). The latter ones behave similar to their piperidine-bridged counterparts (case II). From the decay associated spectra of WS1 (Figure 4b) and WW1 (Figure 12b) it can be concluded that in nonpolar solvents harpooning occurs in WS1 (and SS1), but is absent in WW1 (and SW1).

It is observed that the data points representing CT emissions for WW1 and SW1 (cases I and II) cannot be adequately described by eq 12. As argued before<sup>26,48</sup> the observed curvature in these plots has been interpreted as the result of an increase of the dipole moment of the emissive state. This increase appears to occur over a rather narrowly defined polarity region, which is typically around di-*n*-propyl ether ( $\epsilon = 3.39$ ) and diisopropyl ether ( $\epsilon =$ 3.98). Separately the two regions can well be fitted by a straight line. In the more polar solvents slope values of  $(30-43) \times 10^3$ cm<sup>-1</sup> result in dipole moments of about 28 D, using  $\rho = 6.0$  Å (Table 7). This resembles closely dipoles found with the piperidine counterparts, indicating a similar charge separation distance which is provided by an ECT. The intercepts once more reflect the difference in D–A strength. Taking the lower CCT lines, we find for WW1, SW1, WS1, and SS1 25.31 × 10<sup>3</sup>, 23.6 × 10<sup>3</sup>, 22.87 × 10<sup>3</sup>, and 20.3 × 10<sup>3</sup> cm<sup>-1</sup>. Relative to SS1 this amounts to 0.62, 0.41, and 0.32 eV. The upper CCT lines are 0.18, 0.17, 0.13, and 0.12 eV above the lower ones in, respectively, WW1, SW1, WS1, and SS1. Thus, the ranges of differences in  $\bar{\nu}_{max}$  are in accordance with the electrochemical measurements (Table 2). In the nonpolar region dipole moments of only 16 D are calculated for the red CT emissions. This corresponds well to CCT species, in which the charge separation distance is generally assumed to be 3.5 Å. These flexible systems possess various partly extended and folded conformers. Apparently more than one folded conformer gives rise to CT fluorescence, as was established firmly in WW1, SW1, and WS1, in both OMA and trace data (e.g., Figures 4, 5, 11, and 12).

It is remarkable that systems which possess the same donor and acceptor have such different fluorescence quantum yields (Table 4); e.g., compare WS1 in nonpolar solvents to WS2. We have indications that some of these differences are related to triplet formation of the ECT (Roest and Scherer, unpublished observations). It is likely that the more rigid piperidine systems are more prone to spin degradation.<sup>52</sup> Especially when the extended conformer has a considerable lifetime (in WS1 0.8–1.6 ns versus 5–11 ns in WS2), the folding following charge separation inherent to the harpooning mechanism has to compete with triplet formation, and this will reduce the emissive decay. It is also found that the methoxy series have in general lower quantum yields. This can be explained by the faster decay rates related to the smaller energy gap with the ground state.

3.4. Spectral Shapes. The charge-transfer spectra possessed half-widths  $\Delta \bar{\nu}_{1/2}$  ranging from  $3 \times 10^3$  to  $6 \times 10^3$  cm<sup>-1</sup>, and were negatively skewed (-0.4 < b < -0.1); i.e., they possessed red tails. In the harpooning systems with a type 2 bridge the CCT widths were larger than the ECT widths, whereas with a type 3 bridge the reverse was the case. According to Marcus<sup>38,53</sup> the vibrational contribution to the CT width is frequently dominant. Thus, we hypothesize that the vibrational reorganization parameter is larger in CCT conformations with a type 2 bridge. In polar solvents the ECT width generally increases with solvent polarity. This can be explained by an increase of the solvent reorganization parameter. The CCT widths of SW1, WS1, and SS1 are smallest, (3.7–4.0)  $\times 10^3$  cm<sup>-1</sup>. This may be attributed to a smaller vibrational reorganization parameter in these flexibly bridged systems.

3.5. Concluding Remarks. Time-resolved fluorescence spectra are usually decomposed with the help of a kinetic model (e.g., refs. 25 and 35-37). On the one hand, traces with high temporal resolution are usually measured at a limited number of wavelengths. On the other hand, time-gated OMA data possess a high spectral resolution in combination with a lower temporal resolution. We have shown here that these OMA data can well be analyzed using a triad of the singular value decomposition (to establish the number of components), a spectral model (Eq 11) which produces concentration profiles, and a kinetic model to analyze them. With traces the kinetic model produces decay associated spectra, which need further model assumptions to arrive at the species associated spectra. In both cases the fundamental decomposition problem remains: let A be an invertible matrix, then  $CE^{T} = CAA^{-1}E^{T} = CA(EA^{-T})^{T}$ . In words, a rotation of the spectral or concentration matrix produces exactly the same nonlinear parameters and the same residuals when a spectral or temporal model is used. With highly overlapping spectra there is no clear-cut solution (in particular in cases like that of WW2 in trans-decalin). In principle a spectrotemporal model (using a diagonal A matrix in eq 7) could remove this ambiguity. But this requires data with both adequate temporal and spectral resolution, which preferably lack problems like multiplicative bias.

From the analyses presented here it is concluded that the D-A strength and type of bridge determine photophysical behavior. Solvent polarity can have a pronounced influence on the geometrical structure of the species responsible for what is commonly referred to as exciplex emission. While this has been inferred earlier from studies on flexible systems,<sup>9</sup> our data on semirigid systems now provides unequivocal proof. With moderately polar media ( $\epsilon > 3.5$ ) only ECT emission is found. In nonpolar media harpooning can be found, which depends upon the type of bridge (flexible or semirigid), D-A strength (present with an S acceptor, absent with a W acceptor), solvent polarity (less polar than di-n-butyl ether with a flexible bridge, less polar than *cis*-decalin with a semirigid bridge), and solvent viscosity (Figure 8).

Acknowledgment. Drs. F. C. A. Groen, H. J. W. Spoelder, and J. M. Warman are thanked for critical reading of the text and inspiring discussions. E. P. M. Corten assisted with the programming. Dr. A. H. Holzwarth kindly provided an implementation of the convolution algorithm. H. J. van Ramesdonk, E. P. H. Stegman, and R. J. Willemse are thanked for their contribution to the experiments. This research was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Research (NWO).

Supplementary Material Available: Tables 8S-17S containing all the estimated spectral and kinetic parameters of the 10 compounds, as well as the fraction of the total quantum yield (% of  $\Phi$ , section 2.2.7) (12 pages). Ordering information is given on any current masthead page.

#### **References and Notes**

- Kavarnos, G. J.; Turro, N. J. Chem. Rev. 1986, 86, 401.
- Beens, H.; Knibbe, H.; Weller, A. J. Phys. Chem. 1967, 47, 1183.
- (3)Weller, A. Z. Phys. Chem. Neue Folge 1982, 133, 93.
- (4) Mataga, N.; Okada, T.; Yamamoto, N. Chem. Phys. Lett. 1967, 1, 119.
- (5) Knibbe, H. Charge-transfer complex formation in the excited state. Ph.D. Thesis, Free University of Amsterdam, 1969.
- (6) Masaki, S.; Okada, T.; Mataga, N.; Sakata, Y.; Misumi, S., Bull. Chem. Soc. Jpn. 1976, 49, 1277.

  - Mataga, N.; Murata, Y. J. Am. Chem. Soc. 1969, 91, 3144.
    Mataga, N.; Okada, T.; Masuhara, H.; Nakashima, N.; Sakata, Y.;
- Misumi, S. J. Lumin. 1976, 12/13, 159.
- (9) Mataga, N. Pure Appl. Chem. 1984, 56, 1255.
- (10) Okada, T.; Saito, N.; Mataga, N.; Sakata, Y.; Misumi, S. Bull. Chem. Soc. Jpn. 1977, 50, 331
- (11) Migita, M.; Okada, T.; Mataga, N.; Sakata, Y.; Misumi, S.;
  Nakashima, N.; Yoshihara, K. Bull. Chem. Soc. Jpn. 1981, 54, 3304.
  (12) Okada, T.; Migita, N.; Mataga, N.; Sakata, Y.; Misumi, S. J. Am.
  Chem. Soc. 1981, 103, 4715.
- (13) Nakatani, K.; Okada, T.; Mataga, N.; De Schryver, F. C.; Van der Auweraer, M. Chem. Phys. Lett. 1988, 145, 81.
- (14) Mataga, N.; Nishikawa, S.; Asahi, T.; Okada, T. J. Phys. Chem. 1990, 94, 1443.
- (15) Kroon, J. Rigid donor-bridge-acceptor systems as flexible tools for detection of long-range donor-acceptor interaction. Ph.D. Thesis, University of Amsterdam, 1992
- (16) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. J. Am. Chem. Soc. 1987, 109, 3258.

- (17) Rettig, W.; Haag, R.; Wirz, J. Chem. Phys. Lett. 1991, 180, 216.
- (18) Verhoeven, J. W. Pure Appl. Chem. 1990, 62, 1585.
- (19) Wasielewski, M. R.; Minsek, D. W.; Niemczyk, M. P.; Svec, W. A.; Yang, N. C. J. Am. Chem. Soc. 1990, 112, 2823.
- (20) Nakatani, K.; Okada, T.; Mataga, N.; De Schryver, F. C. Chem. Phys. 1988, 121, 87.
- (21) Wegewijs, B.; Hermant, R. M.; Verhoeven, J. W.; Kunst, A. G. M.; (c1) vogewijs, B., Heinard, K. M., Verhoven, J. V., Kurst, A. G. H.,
   Rettschnick, R. P. H. Chem. Phys. Lett. 1987, 140, 587.
   (22) Wegewijs, B.; Hermant, R. M.; Verhoven, J. W.; De Haas, M. P.;
- Warman, J. M. Chem. Phys. Lett. 1990, 168, 185.
- (23) Borkent, J. H.; De Jong, A. W. J.; Verhoeven, J. W.; De Boer, Th. J. Chem. Phys. Lett. 1978, 57, 530.
- (24) Brouwer, A. M.; Mout, R. D.; Maassen van den Brink, P. H.; Van Ramesdonk, H. J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. Chem. Phys. Lett. 1991, 186, 481.
- (25) Van Stokkum, I. H. M.; Brouwer, A. M.; Van Ramesdonk, H. J.; Scherer, T. Proc. K. Ned. Akad. Wet. 1993, 96, 43.
- (26) Verhoeven, J. W.; Scherer, T.; Willemse, R. J. Pure Appl. Chem. 1993, 65, 1717.
- (27) Anderson, D. H. Compartmental modeling and tracer kinetics; Springer: Berlin, 1983.
- (28) Godfrey, K. Compartmental models and their application; Academic Press: London, 1983.
- (29) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. Purification of laboratory chemicals, 2nd ed.; Pergamon: Oxford, 1980.
  - (30) Van Ramesdonk, H. J.; Verhoeven, J. W. Tek Imager 1989, 1, 2. (31) Eaton, D. F. Pure Appl. Chem. 1988, 60, 1107.
- (32) Hermant, R. Highly fluorescent donor-acceptor systems. Ph.D. Thesis, University of Amsterdam, 1990.
- (33) Golub, G. H.; LeVeque, R. J. Proceedings of the 1979 Army Numerical Analysis and Computer Conference. ARO Report 79-3; 1979; p 1.
  - (34) Kaufman, L. BIT 1975, 15, 49,
  - (35) Nagle, J. F. Biophys. J. 1991, 59, 476.
- (36) Beechem, J. M.; Ameloot, M.; Brand, L. Chem. Phys. Lett. 1985, 120. 466.
- (37) Knutson, J. R.; Beechem, J. M.; Brand, L. Chem. Phys. Lett. 1983, 102.501
  - (38) Marcus, R. A. J. Phys. Chem. 1989, 93, 3078.
- (39) Lakowicz, J. R. Principles of fluorescence spectroscopy; Plenum Press: New York, 1983; Chapter 2.
- (40) Fraser, R. D. B.; Suzuki, E. Anal. Chem. 1969, 41, 37.
- (41) Sevilla, J. M.; Dominguez, M.; Garcia-Blanco, F.; Blazquez, M. Comput. Chem. 1989, 13, 197.
  - (42) Lippert, E. Z. Naturforsch. 1955, 10A, 541.
  - (43) Lippert, E. Z. Electrochem. 1957, 61, 962.
- (44) Mataga, N.; Kaifu, Y.; Koizumi, M. Bull. Chem. Soc. Jpn. 1955, 28, 690
- (45) Mataga, N.; Kaifu, Y.; Koizumi, M. Bull. Chem. Soc. Jpn. 1956, 29, 465.
- (46) Suppan, P. J. Photochem. Photobiol. 1990, 50, 293.
- (47) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D.
- W.; Adams, S. N. J. Am. Chem. Soc. 1966, 88, 3498. (48) Scherer, T.; Willemse, R. J.; Verhoeven, J. W. Recl. Trav. Chim.
- Pays-Bas 1991, 110, 95.
- (49) Schuddeboom, W.; Scherer, T.; Warman, J. M.; Verhoeven, J. W. J. Phys. Chem. 1993, 97, 13092.
- (50) Boens, N.; Andriessen, R.; Ameloot, M.; Van Dommelen, L.; De Schryver, F. C. J. Phys. Chem. 1992, 96, 6331.
- (51) Lowry, T. H.; Schueller-Richardson, K. Mechanism and theory in organic chemistry, 3rd ed.; Harper & Row: New York, 1987; p 139.
- (52) Staerk, H.; Kühnle, W.; Treichel, R.; Weller, A. Chem. Phys. Lett. 1985, 118, 19.
- (53) Gould, I. R.; Farid, S.; Young, R. H. J. Photochem. Photobiol., A 1992, 65, 133.
- (54) Meites, L.; Zuman, P. CRC Handbook series in Organic Electrochemistry; CRC Press: Cleveland, OH, 1976; Vol. 1.
- (55) Berlman, I. B. Handbook of fluorescence spectra of aromatic molecules, 2nd ed.; Academic Press: New York, 1971
- (56) Arnold, D. R.; Maroulis, A. J. J. Am. Chem. Soc. 1976, 98, 5931. (57) Beens, H.; Weller, A. In Molecular Luminescence; Lim, E. C., Ed.; Benjamin: New York, 1969.