Presence and Absence of Excited State Intramolecular Charge Transfer with the Six Isomers of Dicyano-*N*,*N*-dimethylaniline and Dicyano-(*N*-methyl-*N*-isopropyl)aniline

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Supporting Information

ABSTRACT:



The excited state behavior of the six *m*,*n*-dicyano-*N*,*N*-dimethylanilines (mnDCDMA) and *m*,*n*-dicyano-(*N*-methyl-*N*-isopropyl)anilines (mnDCMIA) is discussed as a function of solvent polarity and temperature. The dicyano moiety in these electron donor (D)/acceptor (A) molecules has a considerably larger electron affinity than the benzonitrile subgroup in 4-(dimethylamino)benzonitrile (DMABN). Nevertheless, the fluorescence spectra of the mnDCDMAs and mnDCMIAs in *n*-hexane all consist of a single emission originating from the locally excited (LE) state, indicating that a reaction from LE to an intramolecular charge transfer (ICT) state does not take place. The calculated energies E(ICT), obtained by employing the reduction potential of the dicyanobenzene subgroups and the oxidation potential of the amino substituents trimethylamine $(N(Me)_3)$ and isopropyldimethylamine (iPrNMe₂), are lower than E(LE). The absence of an LE \rightarrow ICT reaction therefore makes clear that the D and A units in the dicyanoanilines are not electronically decoupled. In the polar solvent acetonitrile (MeCN), dual (LE + ICT) fluorescence is found with 24DCDMA and 34DCDMA, as well as with 24DCMIA, 25DCMIA, and 34DCMIA. For all other mnDCDMAs and mnDCMIAs, only LE emission is observed in MeCN. The ICT/LE fluorescence quantum yield ratio $\Phi'(ICT)/\Phi(LE)$ in MeCN at 25 °C is larger for 24DCDMA (1.2) than for 34DCDMA (0.35). The replacement of methyl by isopropyl in the amino substituent leads to a considerable increase of $\Phi'(ICT)/\Phi(LE)$, 8.8 for 24DCMIA and 1.4 for 34DCMIA, showing that the LE \rightleftharpoons ICT equilibrium has shifted further toward ICT. The appearance of an ICT reaction with the 2,4- and 3,4-dicyanoanilines is caused by a relatively small energy gap $\Delta E(S_1, S_2)$ between the two lowest excited singlet states as compared with the other *m*,*n*-dicyanoanilines, in accordance with the PICT model. The observation that the ICT reaction is more efficient for 24DCMIA and 34DCMIA than for their mnDCDMA counterparts is mainly caused by the fact that iPrNMe₂ is a better electron donor than $N(Me)_3$: $E(D/D^+) =$ 0.84 against 1.05 V vs SCE. That ICT also occurs with 25DCMIA, notwithstanding its large $\Delta E(S_1,S_2)$, is due to the substantial amino twist angle $\theta = 42.6^\circ$, which leads to partial electronic decoupling of the D and A subgroups. The dipole moments $\mu_e(ICT)$ range between

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18 D for 34DCMIA and 12 D for 25DCMIA, larger than the corresponding $\mu_e(LE)$ of 16 and 11 D. The difference between $\mu_e(ICT)$ and $\mu_e(LE)$ is smaller than with DMABN (17 and 10 D) because of the noncollinear arrangement of the amino and cyano substituents (different dipole moment directions). The dicyanoanilines that do not undergo ICT, have LE dipole moments between 9 and 16 D. From plots of $\ln(\Phi'(ICT)/\Phi(LE))$ vs 1000/*T*, the (rather small) ICT reaction enthalpies ΔH could be measured in MeCN: 5.4 kJ/mol (24DCDMA), 4.7 kJ/mol (24DCMIA), and 3.9 kJ/mol (34DCMIA). With the mnDCDMAs and mnDCMIAs only showing LE emission, the fluorescence decays are single exponential, whereas for those undergoing an LE \rightarrow ICT reaction the LE and ICT picosecond fluorescence decays are double exponential. In MeCN at 25 °C, the decay times τ_2 have values between 1.8 ps for 24DCMIA and 4.6 ps for 34DCMIA at 25 °C. Longer times are observed at lower temperatures. Arrhenius plots of the forward and backward ICT rate constants k_a and k_d of 25DCMIA in tetrahydrofuran, obtained from the LE and ICT fluorescence decays, give the activation energies $E_a = 4.5$ kJ/mol and $E_d = 11.9$ kJ/mol, i.e., $\Delta H = -7.4$ kJ/mol. From femtosecond transient absorption spectra of 24DCDMA and 34DCDMA at 22 °C, ICT reaction times $\tau_2 = 1/(k_a + k_d)$ of 1.8 and 3.1 ps are determined. By combining these results with the data for the fluorescence decays and $\Phi'(ICT)/\Phi(LE)$, the values $k_a = 49 \times 10^{10} \text{ s}^{-1}$ (24DCDMA) and $k_a = 23 \times 10^{10} \text{ s}^{-1}$ (34DCDMA) are calculated. An LE and ICT excited state absorption is present even at a pump/probe delay time of 100 ps, showing that an LE \rightleftharpoons ICT equilibrium is established.

INTRODUCTION

Of the 19 different cyano(CN)-substituted N,N-dimethylanilines (DMAs), seven molecules have been investigated in connection with the occurrence of a reaction from a locally excited (LE) precursor to an intramolecular charge transfer (ICT) state. A definition of the terms LE and ICT is given in ref 1. For the three DMAs substituted with one CN group (Chart 1), only the para-isomer 4-(dimethylamino)benzonitrile (DMABN) undergoes ICT and emits dual fluorescence from an LE and an ICT state.^{2–7} With the orthoand meta-substituted derivatives 2-(dimethylamino)benzonitrile (oDMABN) and 3-(dimethylamino)benzonitrile (mDMABN), such an ICT reaction accompanied by LE + ICT dual fluorescence has not been observed under any condition of solvent polarity or temperature.^{8,9} This inability to undergo an ICT reaction has been attributed to the fact that the energy gap $\Delta E(S_1, S_2)$ between the two lowest excited singlet states is much larger than for DMABN: 7710 cm^{-1} (oDMABN), 7940 cm^{-1} (mDMABN), and 2700 cm⁻¹ (DMABN), in *n*-hexane, for example.¹⁰

Of the six possible isomers of DMA with two CN-substituents, only for 3,4-dicyano-*N*,*N*-dimethylaniline (34DCDMA) and 3,5-dicyano-*N*,*N*-dimethylaniline (35DCDMA) a possible ICT reaction has been discussed.^{9–18} LE fluorescence, but no ICT emission, was then reported with 34DCDMA and 35DCDMA, even in the strongly polar solvent acetonitrile (MeCN, $\varepsilon^{25} = 36.7$), although fluorescence spectra were not shown.^{9,11–15} In accordance with this observation, the LE fluorescence decays, at a time resolution of ~10 ps, are single exponential with times in the nanosecond range and no indication of a second, shorter picosecond decay time.^{9,11} The absence of ICT emission was, similar to what is described above for oDMABN and mDMABN, explained by the magnitude of $\Delta E(S_1,S_2)$, which, in *n*-hexane, is again much larger than in the case of DMABN: 4360 cm⁻¹ for 34DCDMA and 7200 cm⁻¹ for 35DCDMA, as compared with 2700 cm⁻¹ for DMABN.¹⁰

The photophysical behavior of anilines with three CN-substituents, 2,4,6-tricyano-N,N-dimethylaniline (TCDMA), 2,4, 6-tricyano-N-methylaniline (TCMA), and 2,4,6-tricyanoaniline (TCA), has been investigated by employing photostationary absorption and emission spectra, picosecond fluorescence decays, and femtosecond transient absorption.¹⁵ With these measurements, only a single LE state could be detected for these molecules, without any evidence for the occurrence of an LE \rightarrow ICT reaction, even in a strongly polar solvent such as MeCN.¹⁵ This experimental finding was supported by the results of Chart 1



computations.¹⁵ For pentacyano-*N*,*N*-dimethylaniline (PCDMA) in MeCN and tetrahydrofuran (THF), the fluorescence spectra likewise consist of a single LE emission, and the femtosecond transient absorption spectra only show the presence of a single LE state.¹⁰ In conclusion, similar to the DMABNs and DCDMAs treated above, the absence of an ICT reaction for TCDMA and PCDMA has also been attributed to their large energy gaps $\Delta E(S_{1},S_{2})$, 5370 cm⁻¹ (TCDMA,¹⁵ MeCN) and 7170 cm⁻¹ (PCDMA,¹⁰ MeCN), in accordance with the planar ICT (PICT) model.^{7,9–11,13–15}

As has been discussed before, 9^{-15} the absence of an ICT reaction with the electron donor (D)/acceptor (A) molecules 34DCDMA, 35DCDMA, TCDMA, and PCDMA is at first sight unexpected, because the dicyanobenzene, tricyanobenzene, and pentacyanobenzene A moieties have a considerably larger electron affinity than benzonitrile (the A subunit of DMABN). This can be seen from their reduction potentials $E(A^{-}/A)$.^{10,19} For each of these D/A molecules, under the assumption of weakly interacting D and A subgroups (the twisted ICT (TICT) model),⁶ the calculated energy E(ICT) of the ICT state is lower than the energy $E(S_1,LE)$ of the excited state precursor, in *n*-hexane as well as in MeCN. Under these conditions, an LE \rightarrow ICT reaction should be found: $\Delta H < 0.^{10}$ The fact that such a reaction is not observed^{9-13,15} makes clear that the D and A groups in a hypothetical ICT state of 34DCDMA, 35DCDMA, TCDMA, and PCDMA are not electronically decoupled, as would be required in the TICT approach.6

34DCDMA and 35DCDMA Computations. From computations on 35DCDMA, it has been concluded that its *meta*-CN substituents influence the S₁ as well as the S₂ state, in contrast to DMABN, for which the interaction with CN mainly takes place for S₂.¹⁶ The S₁ and S₂ states of 35DCDMA, with similar dipole moments, are therefore equally stabilized when the solvent polarity increases. This means that the energy gap $\Delta E(S_1,S_2)$,¹⁶ which in the gas phase (calculations) is already much larger than for DMABN,^{20,21} does not become smaller with increasing solvent polarity, explaining why dual emission comparable to that of DMABN is not observed with 35DCDMA. It is then concluded Chart 2

Chart 3



that its fluorescence spectrum is that of a single LE S₁ emission band and that even for 35DCDMA in very polar solvents a S₁(LE) state with planar conformation is favored.¹⁶ In another computation on 34DCDMA and 35DCDMA, it was found that their S₁ states have CT character and that these molecules have a significantly larger energy gap $\Delta E(S_1,S_2)$ than DMABN, explaining the absence of dual fluorescence, again in accordance with the PICT model.¹⁷

In a time-dependent density-functional calculation, without geometry optimization for the excited states, the absence of dual fluorescence of 34DCDMA and 35DCDMA in polar solvents is discussed.¹⁸ These molecules have again a large $\Delta E(S_1, S_2)$ gap, which was taken as an explanation that an ICT reaction does not take place (PICT model). The single S_1 fluorescence band of 34DCDMA is identified as coming from a TICT state, with a dipole moment $\mu_{e}(S_1)$ of 24 D. The energy $E(S_1)$ of 35DCDMA is almost independent of the amino twist angle. This S₁ state has important CT character, as seen from its computed $\mu_{e}(S_{1})$ of 19 D. The Franck–Condon state $S_1(FC)$, reached by excitation of the equilibrated S₀ ground state, is an ICT state with a calculated dipole moment $\mu_{e}(S_{1},abs)$ of 17 D for 34DCDMA and 15 D for 35DCDMA. The $S_2(FC)$ state is claimed to be of LE nature, although $\mu_{e}(S_{2}$, abs) of both molecules is with 16 D, similar to $\mu_{e}(S_{1}, abs)$. $\Delta E(S_{1}, S_{2})$ is hence not reduced by increasing the solvent polarity, an explanation for the absence of an ICT reaction, as mentioned above. In all three calculations, $^{16-18}$ only the S₀ structure was opti-

In all three calculations,^{10–18} only the S_0 structure was optimized, and this structure was subsequently used for the excited states. For the TICT states, a rotation around the *N*-phenyl bond was introduced, leaving the rest of the molecular structure unchanged. Therefore, whereas absorption spectra can be obtained from the calculations, the computed states are not the relaxed S_1 and ICT states from which the fluorescence is emitted.

In the present Article, the photophysics of all six mnDCDMA isomers and *N*-(2,4-dicyanophenyl)azetidine (24DCP4C) is discussed (Chart 2). In addition, the six *m*,*n*-dicyano-(*N*-methyl-*N*-isopropyl)anilines (mnDCMIA) and 2,4-dicyano-*N*-isopropyl-aniline (24DCIA) are studied (Chart 3).

EXPERIMENTAL SECTION

3-Nitro-1,2-dicyanobenzene was treated with HCl in methanol under addition of iron powder, resulting in 2,3-dicyanoaniline. This compound was reacted with dimethylsulfate, producing 23DCDMA (mp 104.4-105.6 °C).^{22a} 23DCMIA was obtained by adding methyldiisopropylamine to a solution of 3-nitro-1,2-dicyanobenzene and triethylamine in N,N-dimethylacetamide at 100 °C, with a final treatment (10 min) under microwave irradiation (CEM, Discover). 24DCDMA (mp 109.0-109.4 °C), 25DCDMA, and 35DCDMA (mp 179.8-180.2 °C) were made in a reaction between the corresponding m,n-dibromoaniline and methyl iodide (MeI) followed by a treatment²³ with CuCN in quinoline or dimethylformamide. 24DCMIA, 25DCMIA, and 35DCMIA (mp 107.1-107.6 °C) were likewise synthesized by adding MeI to a solution of the *m*,*n*-dibromoaniline and isopropyl iodide (iPrI). To obtain 26DCDMA (mp 145.0-145.4 °C) and 34DCDMA, the appropriate *m,n*-dibromoaniline was reacted with dimethysulfate, whereas 26DCMIA resulted from 2,6-dibromoaniline and iPrI in methanol. 34DCMIA was synthesized from 4-fluoro-1,2-dicyanobenzene and methylisopropylamine by microwave irradiation for 3 min at 100 °C. 2,4-Dicyano-*N*-isopropylaniline (24DCIA, mp 98.8–99.1 °C) was made from 2,4-dibromoaniline and iPrI, giving 2,4-dibromo-N-isopropylaniline and a subsequent reaction with CuCN. Finally, 24DCP4C (mp 191.3-191.4 °C) was synthesized from 2,4-dicyano-1-fluorobenzene (24DCF) and azetidine in dimethylsulfoxide. 24DCF was obtained in a reaction between 2,4-dibromo-1-fluorobenzene and CuCN. For all molecules investigated, HPLC was the last purification step. All solvents were chromatographed over Al_2O_3 just prior to use. The solutions, with an optical density between 0.4 and 0.6 for the maximum of the first band in the absorption spectrum, were deaerated by bubbling with nitrogen for 15 min. The measurement and treatment of the fluorescence spectra, quantum yields, nanosecond and picosecond single photon counting decays, and femtosecond transient absorption spectra have been described elsewhere. $^{7,24-28}$ The error limits (data reproducibility) of the total fluorescence quantum yields, extinction coefficients, and fluorescence decay times are estimated at 2-3%. The accuracy of the maxima of the fluorescence and absorption spectra is around 50 cm^{-1} (better for narrow bands). For the separated LE and ICT fluorescence bands, the uncertainty of the fluorescence maxima and quantum yields increases by a factor of 3, as a result of unavoidable errors and intrinsic ambiguity during the band separation procedure.



Figure 1. Crystal structures of 24DCDMA (a,b), 24DCMIA (c,d), 25DCMIA (e,f), and 34DCMIA (g,h). For each molecule, a view from above (a,c,e,g) and one along the axis from the amino group to the dicyanobenzene moiety (b,d,f,h) is presented. The amino twist angle θ is defined as (C(2)C(1)N(7)C(8) + C(6)C(1)N(7)C(9))/2. The pyramidal angle φ is the angle between the vector N(7)C(1) and the plane C(8)N(7)C(9). See Chart 4 and Table 1.

RESULTS AND DISCUSSION

X-ray Crystal Analysis. Results of an X-ray crystal analysis of 24DCDMA (Figure 1a,b), 24DCMIA (Figure 1c,d), 25DCMIA (Figure 1e,f), and 34DCMIA (Figure 1g,h) are listed in Table 1, together with data for DMABN,²⁹ 4-(diisopropylamino)benzonitrile (DIABN,²¹ Figure S1 in Supporting Information (SI)), and 4-(azetidinyl)benzonitrile (P4C),²⁶ included for comparison (Chart 4).

Amino Twist Angle θ . For 34DCMIA a small amino twist angle θ of 2.9° is observed (Figure 1). The presence of an ortho CN-substituent leads to larger angles θ in the dicyanoanilines: 13.9° (24DCDMA), 16.7° (24DCMIA), and 42.6° (25DCMIA). The azetidinyl group in 24DCP4C does not cause such steric hindrance: $\theta = 3.6^{\circ}$. Note that DIABN, with two isopropyl substituents, has a larger twist angle (14.1° and 14.4°) than DMABN (0.0°) and P4C (1.0°). The exceptionally large angle $\theta = 42.6^{\circ}$ of 25DCMIA is a result of the somewhat surprising location of isopropylamino in proximity of the ortho cyano group, different from 24DCDMA, 24DCMIA, and 34DCMIA, in which isopropyl has a position opposite of the *ortho-* or *meta*cyano substituent (see Figure 1).

Amino Pyramidal Angle φ . For the dicyanoanilines with an ortho cyano substituent, the amino pyramidal angle φ (Figure 1) is related with the twist angle θ : 25DCMIA has the largest value for φ (38.4°) as well as for θ (42.6°). For 34DCMIA with θ = 2.9°, φ is nevertheless substantial (18.4°). Also for DMABN and P4C a zero or small twist angle is accompanied by a relatively large φ , 12.1° (DMABN) and 25.8° (P4C) (see Table 1).

Amino–Phenyl Bond N(7)-C(1). The length of the bond N(7)-C(1) between the amino nitrogen and the phenyl ring for 24DCDMA, 24DCMIA, and 34DCMIA (around 136 pm) is similar to that of DMABN (136.5 pm) and somewhat longer than the 133.9 pm for 24DCP4C. With 25DCMIA, a clearly longer bond length of 140.6 pm is found. This increase in N(7)-C(1) is

caused by a larger amino twist angle θ and pyramidality of N(7), and consequently a relatively small value of Σ N, the sum of the angles around N(7), of 344.6° for 25DCMIA, as compared with 359.8° for 24DCDMA, 358.6° for 24DCMIA, and 356.5° for 34DCMIA (Table 1).

Electronic Decoupling of the Amino Group in 25 DCMIA. The exceptionally large amino twist angle $\theta = 42.6^{\circ}$ and pyramidality angle $\varphi = 38.4^{\circ}$ of N(7) in 25DCMIA will lead to an electronic decoupling of the amino and dicyanobenzene subgroups, as shown by the increase of the N(7)–C(1) bond length to 140.6 pm (see above). Such a decoupling can cause a change in the mechanism of the ICT reaction, as encountered with 4-(di-tert-butylamino)benzonitrile³⁰ (DTABN) and 3,5-dimethyl-4-(dimethyl-amino)benzonitrile^{4,9,11,13,21,31} (MMD). This will be further discussed in a subsequent section.

Phenyl Ring. In 24DCDMA, 24DCMIA, and 25DCMIA, the bonds C(1)-C(2) and C(2)-C(3) adjacent to the ortho CNgroup are clearly lengthened as compared with DMABN. For example, for 24DCDMA C(1)-C(2) = 142.9 pm and C(2)-C(3) = 139.4 pm, larger than for DMABN with 140.8 and 137.0 pm.

Absorption and Fluorescence of the Six mnDCDMAs and 24DCP4C at 25 °C. *mnDCDMAs in n-Hexane*. The absorption and fluorescence spectra of the six mnDCDMAs in *n*-hexane at 25 °C are depicted in Figure 2. Two bands appear in the absorption spectra, a lower-energy band of smaller absorbance than the one at higher energy. These bands are attributed to the transition from S₀ to the singlet excited states S₁ and S₂, respectively.^{9–18} The order of the energies of the first absorption band $\tilde{\nu}^{max}(S_{1,abs})$ for the mnDCDMAs in *n*-hexane (Table 2) is: 34 > 24 > 35 > 26 > 23 > 25. The same order has been found for the *m*,*n*-dicyanoanilines in *n*-heptane.³²

The fluorescence spectra consist of a single relatively narrow emission band (half-width $\Delta(1/2) = 3000 - 3650 \text{ cm}^{-1}$) with some vibrational structure, typical for an LE emission. The fluorescence

Table 1.	Data on the	Ground State	Structure of 2	4DCDMA,	24DCMIA,	25DCMIA,	34DCMIA,	and 24DCP4C	from X-ray	Crystal
Analysis'	1									

	24DCDMA	24DCMIA	25DCMIA	34DCMIA	24DCP4C	DMABN ^b	DIABN ^c A	DIABN ^c B	$P4C^d$
N(7) - C(1)	135.4	136.0	140.6	136.9	133.9	136.5	137.6	137.4	136.4
N(7) - C(8)	146.1	146.1	146.9	146.0	146.1	144.8	148.3	148.7	146.5
N(7) - C(9)	145.4	148.2	149.0	147.4	146.6	144.8	147.0	147.9	146.6
C(1) - C(2)	142.9	142.9	141.6	141.1	142.0	140.8	142.0	141.9	140.4
C(1) - C(6)	141.4	142.1	139.7	141.0	141.7	140.8	141.2	141.4	139.8
C(2) - C(3)	139.4	139.5	139.3	138.3	139.8	137.0	137.4	137.1	137.7
C(2) - C(12)	143.3	143.8	143.9		143.3				
C(3) - C(4)	137.5	138.0	137.7	140.5	138.4	138.8	139.1	139.3	139.5
C(3) - C(12)				143.9					
C(4) - C(14)	143.6	143.5		143.3	143.4	142.7	143.7	143.7	143.6
C(4) - C(5)	140.5	139.8	139.2	138.7	140.9	138.8	139.7	139.1	139.2
C(5) - C(6)	136.2	136.6	139.0	137.4	136.6	137.0	137.5	137.6	137.9
C(9) - C(10)		152.3	152.1	151.6	153.3		152.7	152.5	154.2
C(9) - C(11)		152.0	151.5	151.2			152.3	151.5	
C(12)-N(13)	114.7	114.9	114.7	114.6	115.2				
C(14) - N(15)	114.6	114.9	114.5	114.8	115.3	114.5	115.0	114.7	114.4
C(1)-N(7)-C(8)	120.4	121.9	115.0	118.5	135.1	120.6	122.3	122.5	127.4
C(1)-N(7)-C(9)	124.2	121.0	115.2	120.7	130.3	121.5	120.0	120.0	128.3
C(8) - N(7) - C(9)	115.4	115.7	114.4	117.3	94.5	116.4	115.2	114.9	94.1
C(8)-N(7)-C(1)-C(2)	11.4	23.9	19.6 ^e	-8.8	-5.6	-7.7	23.8	-24.9	-22.0
C(9)-N(7)-C(1)-C(6)	16.5	9.6	65.8 ^f	14.6	-1.7	7.7	4.4	-3.9	24.0
twist angle $ heta^g$	13.9	16.7	42.6	2.9	3.6	0.0	14.1	14.4	1.0
ΣN^h	359.8	358.6	344.6	356.5	359.9	358.5	357.5	357.5	349.8
pyramidal angle ω^i	2.4	11.3	38.4	18.4	2.3	12.1	15.1	15.2	25.8

^{*a*} The structural data for DMABN, DIABN, and P4C are included for comparison. ^{*b*} Ref 29 (253 K). ^{*c*} Ref 21 (293 K). ^{*d*} Crystal structure data of P4C have appeared in ref 26, under the name AZABN. ^{*e*} C(8)N(7)C(1)C(6), see Chart 4. ^{*f*} C(9)N(7)C(1)C(2), see Chart 4. ^{*g*} Twist angle θ : (C(2)C(1)N(7)C(8) + C(6)C(1)N(7)C(9))/2 (Chart 4 and Figure 1). ^{*h*} Sum of the angles around the amino nitrogen. ^{*i*} Pyramidal angle φ : angle between the vector N(7)C(1) and the plane C(8)N(7)C(9) (Chart 4 and Figure 1).

Chart 4



remains single down to -95 °C. It originates from an LE state, as there is no indication of an additional red-shifted ICT fluorescence. This is clear evidence that an LE \rightarrow ICT reaction does not take place with the six DCDMAs in *n*-hexane at 25 °C.

The fluorescence quantum yields $\Phi(LE)$ range between 0.07 (24DCDMA and 26DCDMA) and 0.31 (25DCDMA), with large intersystem crossing yields $\Phi(ISC)$: 0.78, 0.81, and 0.54 (Table 2). The process of internal conversion (IC) from S₁(LE) directly to S₀ is relatively important, with yields $\Phi(IC)$ between 0.12 (26DCDMA) and 0.46 (35DCDMA), see Table 2.

24DCP4C in *n*-Hexane. The fluorescence spectrum of 24DCP4C in *n*-hexane at 25 °C (Figure S2a in SI) consists of a single LE emission, similar to what has been observed^{11–13,26,33} with its parent compound P4C (Table 2).

mnDCDMAs in MeCN. The absorption and fluorescence spectra of the six mnDCDMAs in MeCN at 25 °C are shown in Figure 3 (Table 3). The absorption spectra in this polar solvent are red-shifted relative to those in *n*-hexane (cf. Figure 2, Table 2). The order of the energies of the first absorption band $\tilde{\nu}^{max}(S_1,abs)$ for the mnDCDMAs in MeCN (Table 3) is: $24 > 34 > 26 \approx 35 > 23 > 25$. A similar order has been reported for the *m,n*-dicyanoanilines in MeCN and H₂O, as well as in 95% C₂H₅OH.^{32,22b} This means that there is in this respect no substantial influence of steric hindrance between the dimethylamino group and an *ortho*-cyano substituent in the mnDCDMAs with mn = 23, 24, 25, and 26. It was stated in ref 22b that this order cannot be explained in terms of resonance theory, as discussed previously.³⁵

The fluorescence spectra of four of the mnDCDMAs (23-, 25-, 26-, and 35DCDMA) consist of a single unstructured emission



Figure 2. Fluorescence (LE) and absorption (Abs) spectra of the six m,n-dicyano-N,N-dimethylanilines mnDCDMA (Chart 2) in n-hexane at 25 °C. The fluorescence spectra are attributed to the single emission from a locally excited (LE) state.

Table 2. Data Obtained from the Fluorescence and Absorption Spectra of the Six mnDCDMAs, 24DCP4C, and P4C in *n*-Hexane at 25 $^{\circ}$ C

	23DCDMA	24DCDMA	25DCDMA	26DCDMA	34DCDMA	35DCDMA	24DCP4C	P4C ^a
$\tilde{v}^{\max}(\text{LE}) [\text{cm}^{-1}]$	24410	26370	24340	25180	26470	25910	27100, 26040	29330
$\Delta(1/2)(\mathrm{LE})^b [\mathrm{cm}^{-1}]$	3400	3410	3120	3030	3650	3000	3220	3470
$\Delta(1/4)(\text{LE})^{c} [\text{cm}^{-1}]$	4610	4650	4300	4110	4940	4150	4370	4710
$\Phi(LE)$	0.13	0.065	0.31	0.066	0.17	0.095		0.26
$\Phi(\text{ISC})^d$	0.53 ± 0.08	0.78 ± 0.04	0.54 ± 0.03	0.81 ± 0.03	0.57 ± 0.06	$\textbf{0.45} \pm \textbf{0.07}$		0.67
$\Phi(\mathrm{IC})^e$	0.34	0.16	0.15	0.12	0.26	0.46		0.07
$\tilde{v}^{\max}(S_1, abs) [cm^{-1}]$	27570	29540	27420	27830	29670	28450	29330	31110
$\varepsilon^{\max}(S_1, abs) [M^{-1} cm^{-1}]$	f	5020	4410	g	f	f		
$\tilde{v}^{\max}(S_{2}$, abs) [cm ⁻¹]	36100	34390	36740	34450	34030	35760	34600	35670
$\varepsilon^{\max}(S_{2,abs}) [M^{-1}cm^{-1}]$		26220	9800					29950
$E(S_1)^h [cm^{-1}]$	25850	27880	25590	26280	28000	26900	27720	31060
$\Delta E(S_1,S_2)^i [\text{cm}^{-1}]$	8530	4850	9320	6620	4360	7310	5270	4560
a Same a C a C b Early and the at	half an arritory	of the total LE	Auguarana	and ^c Early and del		rimerum of the to	tal IE Amanagaan	hand

^{*a*} See ref 26. ^{*b*} Full width at half-maximum of the total LE fluorescence band. ^{*c*} Full width at quarter-maximum of the total LE fluorescence band. ^{*d*} Measurements (at 23 °C) as in refs 26 and 34. ^{*e*} $\Phi(IC) = 1 - \Phi(LE) - \Phi'(ICT) - \Phi(ISC)$. ^{*f*} Not sufficiently soluble in *n*-hexane. ^{*g*} Not enough substance available. ^{*h*} Crossing point of the normalized fluorescence and absorption spectra. ^{*i*} Energy difference $\tilde{v}^{max}(S_{2,a}bs) - \tilde{v}^{max}(S_{1,a}bs)$.

band (Figure 3a,c,d,f), with an asymmetric shape similar to that of the LE fluorescence of these molecules in *n*-hexane (Figure 2a, c,d,f) and that of, e.g., TCDMA¹⁵ in MeCN. The bands are therefore likewise assigned to the LE state. It should be noted, however, that the fluorescence band of 25DCDMA (Figure 3c) is somewhat broader than that of the other three isomers, as seen from its half-width $\Delta(1/2) = 4580 \text{ cm}^{-1}$ and quarter-width $\Delta(1/4) = 6550 \text{ cm}^{-1}$ (Table 3). The overall fluorescence quantum yield of 25DCDMA (0.046) is lower than that of 23DCDMA (0.283), 26DCDMA (0.096), and 35DCDMA (0.162) (Table 3), an additional indication that with 25DCDMA in MeCN an LE \rightarrow ICT reaction is starting to occur. This interpretation is strengthened by the appearance of an ICT emission band in the spectrum of the related compound 25DCMIA in MeCN (Figure 5c, below).

With 24DCDMA and 34DCDMA in MeCN, in contrast, an additional fluorescence band is present at the low-energy side of the LE emission (Figure 3b,e), and the band is attributed to the ICT state. The half-width $\Delta(1/2)$ of the overall fluorescence



Figure 3. Fluorescence (LE or LE + ICT) and absorption (Abs) spectra of the six *m,n*-dicyano-*N*,*N*-dimethylanilines mnDCDMA (Chart 2) in acetonitrile (MeCN) at 25 °C. The fluorescence spectra are attributed to the emission from a locally excited (LE) state, except for those of 24DCDMA and 34DCDMA, which show dual fluorescence from an LE and an intramolecular charge transfer (ICT) state (see text). The ICT emission band has been obtained by subtraction with the shifted LE fluorescence spectrum in *n*-hexane (Figure 2).

Table 3.	Data Obtained from the Fluorescence and Absorption Spectra of the Six mnDCDMAs, 24DCP4C, and P4C in MeCN at
25 °C	

	23DCDMA	24DCDMA	25DCDMA	26DCDMA	34DCDMA	35DCDMA	24DCP4C	P4C ^a
$\tilde{v}^{\max}(\text{LE}) \ [\text{cm}^{-1}]$	21180	23880	21070	23170	23040	22510	24580	27610
$\tilde{v}^{\max}(\text{LE}) [\text{cm}^{-1}]$	-	19400	-	-	19160	-	-	19940
$\Delta(1/2)(\mathrm{flu})^b [\mathrm{cm}^{-1}]$	4270	8670	4580	3420	4940	3930	3720	3680
$\Delta(1/2)(\text{LE})^{c} [\text{cm}^{-1}]$	4270	4200	4580	3420	4300	3930	3720	3640
$\Delta(1/2)(\operatorname{ICT})^d [\operatorname{cm}^{-1}]$	-	4960	-	-	6800	-	-	4980
$\Delta(1/4)(\mathrm{flu})^e [\mathrm{cm}^{-1}]$	5680	10700	6550	4830	7450	5530	5100	12530 ^f
$\Delta(1/4)(\text{LE})^g [\text{cm}^{-1}]$	5680	5750	6550	4830	5970	5530	5100	5340
$\Delta(1/4)(\mathrm{ICT})^{h}[\mathrm{cm}^{-1}]$	-	7010	-	-	9630	-	-	7130
$\Phi(LE)$	0.28	0.013	0.046	0.096	0.022	0.16	0.28	0.034
$\Phi'(ICT)$	0	0.016	0	0	0.0077	0	0	0.017
$\Phi'(ICT)/\Phi(LE)$	0	1.2	0	0	0.35	0	0	0.70
$\Phi(\mathrm{ISC})^i$	0.08 ± 0.02	0.69 ± 0.02	$\textbf{0.08} \pm \textbf{0.01}$	0.90 ± 0.01	0.09 ± 0.01	0.57 ± 0.02		0.90
$\Phi(IC)^{j}$	0.64	0.28	0.87	0.0	0.88	0.27		0.05
$\tilde{v}^{\max}(S_1, abs) [cm^{-1}]$	26770	29000	26490	27440	28500	27350	28900	
$\varepsilon^{\max}(S_1,abs) [M^{-1} cm^{-1}]$	4050	5230	4100	3520	6500	2900		
$\tilde{v}^{\max}(S_{2}abs) [cm^{-1}]$	35730	33830	36600	34250	33100	34850	33900	34290
$\varepsilon^{\max}(S_{2}abs) [M^{-1} cm^{-1}]$	9470	25930	8420	8320	23320	12890		27700
$E(S_1)^k [cm^{-1}]$	24020	26680	23900	25130	25930	24910	26690	30600
$\Delta E(S_1,S_2)^l [\mathrm{cm}^{-1}]$	8960	4870	10110	6810	4600	7500	5000	
			1					

^{*a*} See ref 26. There, $\Phi'(ICT) = 0.034$ and $\Phi(LE) = 0.017$, at 20 °C. ^{*b*} Full width at half-maximum (fwhm) of the total fluorescence band. ^{*c*} Fwhm for the separated LE band. ^{*d*} Fwhm for the separated ICT band. ^{*c*} Full width at quarter-maximum (fwqm) of the total fluorescence band. ^{*f*} Separated LE and ICT bands. ^{*g*} Fwqm for the separated LE band. ^{*h*} Fwqm for the separated ICT band. ^{*i*} Measurements (at 23 °C) as in refs 26 and 34. ^{*j*} $\Phi(IC) = 1 - \Phi(LE) - \Phi'(ICT) - \Phi(ISC)$. ^{*k*} Crossing point of the normalized fluorescence and absorption spectra. ^{*l*} Energy difference $\tilde{\nu}^{max}(S_{2,2}abs) - \tilde{\nu}^{max}(S_{1,2}abs)$.



Figure 4. Fluorescence (LE) and absorption (Abs) spectra of the six m,n-dicyano-(N-methyl-N-isopropyl)anilines mnDCMIA (Chart 3) in n-hexane at 25 °C. The fluorescence spectra are attributed to the single emission from a locally excited (LE) state.

band is very large for 24DCDMA (8670 cm⁻¹), larger than for 34DCDMA (4940 cm⁻¹), with a corresponding difference for $\Delta(1/4)$: 10 700 and 7450 cm⁻¹ (Table 3). These spectra have an ICT/LE fluorescence quantum yield ratio $\Phi'(ICT)/\Phi(LE)$ of 1.2 (24DCDMA) and 0.35 (34DCDMA), see Table 3. The LE fluorescence quantum yield $\Phi(LE)$ of 24DCDMA (0.013) and 34DCDMA (0.022) is relatively low (Table 3), due to the quenching by the ICT reaction. The yield $\Phi'(ICT)$ is larger for 24DCDMA (0.016) than for 34DCDMA (0.0077), a further indication, besides $\Phi'(ICT)/\Phi(LE)$, that for the former molecule the LE \rightleftharpoons ICT equilibrium has shifted toward the ICT state. As the fluorescence band of 24DCDMA fully covers the visible spectrum (half-width $\Delta(1/2) = 8670$ cm⁻¹, between 16970 and 25 640 cm⁻¹), this molecule in MeCN is a so-called white light emitter, similar to crystal violet lactone (CVL) in an ethyl acetate/MeCN mixture.³⁶

The intersystem crossing yield $\Phi(ISC)$ of the mnDCDMAs is small for mn = 23 (0.08), mn = 25 (0.08), and mn = 34 (0.09) but large for mn = 24 (0.69, via ICT), mn = 26 (0.90), and mn = 35 (0.57), see Table 3, without any obvious correlation with the absence or presence of an ICT emission. The same is the case for the internal conversion yield $\Phi(IC)$, being zero for mn = 26 (0.00), but clearly larger for the other mnDCDMAs.

24DCP4C in MeCN. The fluorescence spectrum of 24DCP4C in MeCN at 25 °C (Figure S2b in SI) consists of a single LE emission, clearly different from the dual LE + ICT fluorescence of 24DCDMA in this solvent (Figure 3b). This is at first sight surprising, in view of the similar spectral properties, such as the energy gap $\Delta E(S_1,S_2)$ of the two molecules (Table 3), as will be discussed in the next section.

Energy Gap $\Delta E(S_1,S_2)$ and ICT Reactions with mnDCDMA in MeCN. An inspection of the energy gaps $\Delta E(S_1,S_2)$ of the

mnDCDMAs (Table 3) reveals that the two mnDCDMAs clearly showing ICT fluorescence in MeCN at 25 °C (Figure 3b,e) have the smallest gaps (4870 cm⁻¹ for 24DCDMA and 4600 cm⁻¹ for 34DCDMA), as compared with the molecules only showing LE emission, with much larger gaps $\Delta E(S_1,S_2)$: 8960 cm⁻¹ (23DCDMA), 10 110 cm⁻¹ (25DCDMA), 6810 cm⁻¹ (26DCDMA), and 7500 cm⁻¹ (35DCDMA). A similar correlation between the magnitude of $\Delta E(S_1,S_2)$ and the occurrence (DMABN, 2700 cm⁻¹, in *n*-hexane)²¹ or absence (oDMABN, mDMABN, TCDMA, and PCDMA) of an LE \rightarrow ICT reaction has been found before, as mentioned in the Introduction.^{7,9-11,13-15,21} This correlation is an essential part of the PICT model.^{10,12-14,21,24,37}

24DCP4C and P4C. An Argument in Favor of PICT. The absence of the ICT fluorescence with 24DCP4C in contrast to its presence with 24DCDMA in MeCN at 25 °C (Table 3), notwithstanding the practically identical $\Delta E(S_1,S_2)$, is reminiscent of the strong reduction of the efficiency of the LE \rightarrow ICT reaction for P4C in MeCN as compared with DMABN.^{7,11-13,33,38,39} The very low ICT efficiency of P4C has been attributed to a larger amino nitrogen inversion barrier than that of DMABN, an important argument against the validity of the TICT model.^{11-13,26,38,39} This argument is also valid here for 24DCP4C as compared with 24DCDMA.

Absorption and Fluorescence of the Six mnDCMIAs and 24DCIA at 25 °C. mnDCMIAs and 24DCIA in n-Hexane. The absorption and fluorescence spectra of the six mnDCMIAs in *n*-hexane at 25 °C are presented in Figure 4 (Table 4). The absorption spectra consist of two bands, again attributed to $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, as in the case of the mnDCDMAs (Table 2). The energy gap $\Delta E(S_1,S_2)$ of the mnDCMIAs (Table 4) is somewhat $(60-740 \text{ cm}^{-1})$ smaller than that of the corresponding

Table 4. Data Obtained from the Fluorescence and Absorption	1 Spectra of the Six mnDCMIAs and 24DCIA in n -Hexane at 25 $^\circ$ C
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	23DCMIA	24DCMIA	25DCMIA	26DCMIA	34DCMIA	35DCMIA	24DCIA
$\tilde{\nu}^{\max}(LE) [cm^{-1}]$	23910	25630	23730	24640	25940	25300	27100
$\Delta(1/2)(\mathrm{LE})^a$	3470	3920	3510	3200	3580	3160	3130
$\Delta(1/4)(\text{LE})^b$	4780	5450	4850	4430	4890	4300	4320
$\Phi(LE)$	0.13	0.061	0.27	0.032	0.16	0.082	
$\Phi(ISC)^{c}$	0.59 ± 0.06	0.85 ± 0.02	0.56 ± 0.05	0.78 ± 0.03	0.70 ± 0.04		
$\Phi(\mathrm{IC})^d$	0.28	0.09	0.17	0.19	0.14		
$\tilde{\nu}^{\max}(S_1, abs) [cm^{-1}]$	27270	29230	27060	27710	29280	28050	29260
$\varepsilon^{\max}(S_1, abs) [M^{-1} cm^{-1}]$	3510	5130	3970	2170	4410	2810	
$\tilde{\nu}^{\max}(S_{2j}abs) [cm^{-1}]$	35560	34020	36300	33590	33680	35280	35580
$\varepsilon^{\max}(S_{2}$,abs) $[M^{-1} cm^{-1}]$	10920	24470	9290	5410	22750	15400	
$E(S_1)^e [cm^{-1}]$	25540	27460	25290	25990	27590	26480	28430
$\Delta E(S_1,S_2)^f[\mathrm{cm}^{-1}]$	8290	4790	9240	5880	4400	7230	6320

^{*a*} Full width at half-maximum of the total LE fluorescence band. ^{*b*} Full width at quarter-maximum of the total LE fluorescence band. ^{*c*} Measurements (at 23 °C) as in refs 26 and 34. ^{*d*} Φ (IC) = 1 – Φ (LE) – Φ' (ICT) – Φ (ISC). ^{*c*} Crossing point of the normalized fluorescence and absorption spectra. ^{*f*} Energy difference $\tilde{\nu}^{max}(S_{2r}abs) - \tilde{\nu}^{max}(S_{1r}abs)$.

mnDCDMAs (Table 2), except for 34DCMIA with a slightly large gap (+40 cm⁻¹). A similar observation that the introduction of an isopropyl substituent causes a decrease of $\Delta E(S_1,S_2)$ has previously been made for the series DMABN, 4-(isopropylmethylamino)-benzonitrile (IMABN), and 4-(diisopropylamino)benzonitrile (DIABN), leading to the appearance of an ICT reaction with dual LE + ICT fluorescence for IMABN and DIABN, even in *n*-hexane.⁴⁰

The fluorescence spectra of all six mnDCMIAs in *n*-hexane at 25 °C (Figure 4) and down to -95 °C consist of a single band, with some vibrational structure, as also observed with the mnDCDMAs (Figure 2). This band is again attributed to LE, as an additional ICT emission is not found. The same is the case for 24DCIA in *n*-hexane (Figure S3a in SI). The fluorescence quantum yields $\Phi(LE)$ have values between 0.032 (26DCMIA) and 0.27 (25DCMIA). The yields $\Phi(ISC)$ range between 0.56 (25DCMIA) and 0.85 (24DCMIA), from which $\Phi(IC)$ is calculated: from 0.09 (24DCMIA) to 0.28 (23DCMIA) (Table 4). These results are comparable to those obtained with the mnDCDMAs (Table 2).

mnDCMIAs and 24DCIA in MeCN. The absorption and fluorescence spectra of the six mnDCMIAs in MeCN at 25 °C are presented in Figure 5 (Table 5).

26DCMIA, 35DCMIA, and 24DCIA (LE). With 26DCMIA, 35DCMIA (Figure 5d,f), and 24DCIA (Figure S3b in SI), a single fluorescence band is observed, with the characteristic asymmetric shape of an LE emission, comparable to the LE spectra of 26DCDMA and 35DCDMA in MeCN (Figure 3d,f).

24DCMIA and 34DCMIA (LE + ICT). 24DCMIA and 34DCMIA in MeCN (Figure 5b,e), however, show dual LE + ICT fluorescence, with a ratio $\Phi'(ICT)/\Phi(LE)$ of 8.8 and 1.4, respectively (Table 5). Note that these ratios are much larger than those of the corresponding mnDCDMAs: 1.2 (24DCDMA) and 0.35 (34DCDMA) in MeCN (Figure 3b,e and Table 3). This enhancement in ICT efficiency, caused by the introduction of an isopropyl substituent into the amino group, is similar to that found for IMABN and DIABN as compared with DMABN,⁴⁰ as discussed above.

With 34DCMIA, the emission half-width is exceptionally large, $\Delta(1/2) = 9480 \text{ cm}^{-1}$ (Figure 5e and Table 5), as with 24DCDMA in MeCN (Figure 3b). The fluorescence of these

molecules extends over the entire visible spectrum, from 14 700 to 24 180 cm⁻¹, making them potential white-light emitters, similar to what has been reported for CVL.³⁶

25DCMIA (LE + ICT). MeCN. With 25DCMIA in MeCN at 25 °C, dual LE + ICT fluorescence is observed (Figure 5c), but with a smaller ratio $\Phi'(\text{ICT})/\Phi(\text{LE})$ (2.7) than for 24DCMIA (8.8) (Figure 5b) under these conditions (Table 5). The emission spectrum of 25DCMIA is broader ($\Delta(1/2) = 6040 \text{ cm}^{-1}$, $\Delta(1/4)$ = 8630 cm⁻¹) than the LE bands of 26DCMIA $(3950 \text{ cm}^{-1}, 5620 \text{ cm}^{-1})$ and 35DCMIA (4110 cm⁻¹) 5740 cm^{-1}), see Figure 5c,d and Table 5. Also, the spectral shape is different from an asymmetric LE emission, more resembling a typical symmetric ICT fluorescence band, such as for DMABN in MeCN.⁷ The overall fluorescence spectrum of 25DCMIA in MeCN can therefore be separated into its LE + ICT contributions, resulting in a ratio $\Phi'(ICT)/\Phi(LE) = 2.7$ (Figure 5c, Table 5). The presence of dual LE + ICT emission is supported by the increase of $\Phi'(ICT)/\Phi(LE)$ to 4.6, upon cooling to $-45 \,^{\circ}$ C (Figure 6b). In Figure 6a,c it is shown that for 24DCMIA and 34DCMIA in MeCN at -45 °C $\Phi'(ICT)/$ $\Phi(LE)$ has likewise become larger (21.7 and 2.1) than at 25 °C (8.8 and 1.4), see Table 5.

23DCMIA (*LE* + *I*C7?). The emission band of 23DCMIA is also broader ($\Delta(1/2) = 5110 \text{ cm}^{-1}$; $\Delta(1/4) = 7230 \text{ cm}^{-1}$) and less asymmetric than the LE spectrum of 26DCMIA (3950 cm⁻¹; 5620 cm⁻¹) and 35DCMIA (4110 cm⁻¹; 5740 cm⁻¹), although smaller than for 25DCMIA (6040 cm⁻¹; 8630 cm⁻¹). Nevertheless, a spectral separation was not attempted. It should, however, be concluded that most likely a small amount of additional ICT fluorescence is present with 23DCMIA in MeCN at 25 °C, pointing to an incipient ICT reaction.

ICT and Energy Gap $\Delta E(S_1,S_2)$ in MeCN. 24DCMIA and 34DCMIA. The appearance of an ICT emission with 24DCDMA and 34DCDMA in MeCN, different from the other four DCDMAs, was attributed above to their relatively small energy gap $\Delta E(S_1,S_2)$. With the mnDCMIAs in MeCN, 24DCMIA and 34DCMIA likewise have the smallest $\Delta E(S_1,S_2)$ gap: 4690 and 4550 cm⁻¹. The decrease of $\Delta E(S_1,S_2)$ in MeCN of the mnDCMIAs as compared with the mnDCDMAs (Tables 3 and 5) is, however, quite small: only 180 cm⁻¹ for 24DCMIA and 50 cm⁻¹ for 34DCMIA. An influence of



Figure 5. Fluorescence (LE or LE + ICT) and absorption (Abs) spectra of the six *m*,*n*-dicyano-(*N*-methyl-*N*-isopropyl)anilines mnDCMIA (Chart 3) in acetonitrile (MeCN) at 25 °C. The fluorescence spectra are attributed to the emission from a locally excited (LE) state, except for those of 24DCDMA, 25DCDMA, and 34DCDMA, which show dual fluorescence from an LE and an intramolecular charge transfer (ICT) state (see text). The ICT emission band has been obtained by subtraction with the shifted LE fluorescence spectrum in *n*-hexane (Figure 4).

Table 5. Data Obtained from the Fluorescence and Abso	orption Spectra of the Six n	nnDCMIAs and 24DCIA in MeCN at 25 $^\circ$	С
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$\vec{v}^{max}(LE) [cm^{-1}]$ 2103023620220602252022510223202590 $\vec{v}^{max}(LT) [cm^{-1}]$.1943019220.17280 $\Delta(1/2)(lfu)^a [cm^{-1}]$ 5110484060403950948041103430 $\Delta(1/2)(LE)^b [cm^{-1}]$ 5110418039603950476041103430 $\Delta(1/2)(LC)^c [cm^{-1}]$.46805150.5320 $\Delta(1/4)(fu)^d [cm^{-1}]$ 72307300863056201157057404750 $\Delta(1/4)(LE)^c [cm^{-1}]$ 7230594055605620661057404750 $\Delta(1/4)(LC)^f [cm^{-1}]$ 723059405560562066105740. $\Delta(1/4)(LC)^f [cm^{-1}]$.674072807420 $\Delta(1/4)(LC)^f [cm^{-1}]$.674072807420 $\Delta(1/4)(LC)^f [cm^{-1}]$ 67407280 $\Delta(1/4)(LC)^f [cm^{-1}]$ $\Delta(1/4)(LC)^f [cm^{-1}]$ $\Delta(1/4)(LC)^f [cm^{-1}]$ $\Phi(LC)^h$ </th <th></th> <th>23DCMIA</th> <th>24DCMIA</th> <th>25DCMIA</th> <th>26DCMIA</th> <th>34DCMIA</th> <th>35DCMIA</th> <th>24DCIA</th>		23DCMIA	24DCMIA	25DCMIA	26DCMIA	34DCMIA	35DCMIA	24DCIA
$\vec{v}^{max}(\Gamma T) [cm^{-1}]$.<1943019220.17280 $\Delta(1/2)(fh)^a [cm^{-1}]$ 5110484060403950948041103430 $\Delta(1/2)(LE)^b [cm^{-1}]$ 5110418039603950476041103430 $\Delta(1/2)(LC)^c [cm^{-1}]$.46805150.5320 $\Delta(1/4)(fhu)^d [cm^{-1}]$ 72307300863056201157057404750 $\Delta(1/4)(LE)^c [cm^{-1}]$ 7230594055605620661057404750 $\Delta(1/4)(LC)^{f} [cm^{-1}]$ 723059407280.7420 $\Delta(1/4)(LC)^{f} [cm^{-1}]$.67407280.0.00540.20. $\Phi(LE)$ 0.170.00250.00330.6110.00540.20. $\Phi'(ICT)^{f} (LC)^{f}$ 08.82.701.400 $\Phi(ISC)^{S}$ 0.19 ± 0.010.83 ± 0.020.12 ± 0.010.56 ± 0.020.22 ± 0.02 $\Phi(ICD)^{f}$ 0.650.150.850.360.77 $\tilde{v}^{max}(S_1 abs) [cm^{-1}]$ 3430530037903270714028305300 $\tilde{v}^{max}(S_1 abs) [cm^{-1}]$ 352103520361703349032830344703540 $\tilde{v}^{max}(S_2 abs) [cm^{-1}]$ 95702421081704690253801431024220 $E^{max}(S_1 abs) [M^{-1} cm^{-1}]$ 6668 <td>$\tilde{v}^{\max}(\text{LE}) [\text{cm}^{-1}]$</td> <td>21030</td> <td>23620</td> <td>22060</td> <td>22520</td> <td>22510</td> <td>22320</td> <td>25960</td>	$\tilde{v}^{\max}(\text{LE}) [\text{cm}^{-1}]$	21030	23620	22060	22520	22510	22320	25960
$\Delta(1/2)(fh)^a$ [cm ⁻¹]5110484060403950948041103430 $\Delta(1/2)(LE)^b$ [cm ⁻¹]5110418039603950476041103430 $\Delta(1/2)(LCT)^c$ [cm ⁻¹]-46805150-5320 $\Delta(1/4)(fh)^d$ [cm ⁻¹]72307300863056201157057404750 $\Delta(1/4)(LE)^c$ [cm ⁻¹]7230594055605620661057404750 $\Delta(1/4)(LCT)^{f}$ [cm ⁻¹]-67407280-7420 $\Phi(LE)$ 0.170.00250.00330.0610.00540.20- $\Phi'(ICT)/\Phi(LE)$ 08.82.701.400 $\Phi'(ICT)^{h}$ 0.650.150.850.360.77 $\Phi(LS)^s$ 0.19 ± 0.010.83 ± 0.020.21 ± 0.010.58 ± 0.02221 ± 0.022709028840 $\Phi'(ICT)^h$ 6650.150.850.360.77 $\Psi^{max}(S_1 abs) [cm-1]$ 3430330037903270714028303300 $\mu^{max}(S_2 abs) [cm-1]$ 35210335203617033490328303447033540 $\mu^{max}(S_2 abs) [M^{-1} cm^{-1}]$ 352102648025080257702430027600 $\mu^{max}(S_1 bas) [M^{-1} cm^{-1}]$ 600264802508025770243027600	$\tilde{v}^{\max}(ICT) [cm^{-1}]$	-	19430	19220	-	17280	-	-
$\Delta(1/2)(LE)^b [cm^{-1}]$ 5110418039603950476041103430 $\Delta(1/2)(LCT)^c [cm^{-1}]$ -46805150-5320 $\Delta(1/4)(fu)^d [cm^{-1}]$ 72307300863056201157057404750 $\Delta(1/4)(LE)^c [cm^{-1}]$ 7230594055605620661057404750 $\Delta(1/4)(LCT)^f [cm^{-1}]$ -67407280-7420 $\Phi(LE)$ 0.170.00250.00330.6610.00540.200 $\Phi'(ICT)/\Phi(LE)$ 08.82.701.400 $\Phi'(ICT)/\Phi(LE)$ 0.19 ± 0.010.83 ± 0.020.12 ± 0.010.58 ± 0.020.22 ± 0.02- $\Phi(ICC)^h$ 0.650.150.850.360.77 $\Psi^{max}(S_habs)[cm^{-1}]$ 3430350037903270714028303304 $\Psi^{max}(S_abs)[cm^{-1}]$ 3521033520361703349032830344703540 $\xi^{max}(S_abs)[M^{-1}cm^{-1}]$ 95702421081704690253801431024220 $\xi^{max}(S_abs)[M^{-1}cm^{-1}]$ 24260264802508025080257702473027007700	$\Delta(1/2)(\mathrm{flu})^a[\mathrm{cm}^{-1}]$	5110	4840	6040	3950	9480	4110	3430
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta(1/2)(\mathrm{LE})^{b} [\mathrm{cm}^{-1}]$	5110	4180	3960	3950	4760	4110	3430
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta(1/2)(\mathrm{ICT})^{c} [\mathrm{cm}^{-1}]$	-	4680	5150	-	5320	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta(1/4)(\mathrm{flu})^d [\mathrm{cm}^{-1}]$	7230	7300	8630	5620	11570	5740	4750
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Delta(1/4)(\text{LE})^e [\text{cm}^{-1}]$	7230	5940	5560	5620	6610	5740	4750
$\Phi(LE)$ 0.170.00250.00330.0610.00540.20 $\Phi'(ICT)$ 00.0220.02500.007700 $\Phi'(ICT)/\Phi(LE)$ 08.82.701.400 $\Phi(ISC)^g$ 0.19 \pm 0.010.83 \pm 0.020.12 \pm 0.010.58 \pm 0.020.22 \pm 0.02 $\Phi(IC)^h$ 0.650.150.850.360.77 $\tilde{\nu}^{max}(S_{1,abs})[cm^{-1}]$ 26560288302633027930282702709028840 $\tilde{\nu}^{max}(S_{2,abs})[m^{-1}cm^{-1}]$ 3430530037903270714028305300 $\tilde{\nu}^{max}(S_{2,abs})[m^{-1}]$ 35210335203617033490328303447033540 $\tilde{\nu}^{max}(S_{2,abs})[m^{-1}]$ 95702421081704690253801431024220 $E(S_1)^i[cm^{-1}]$ 24260264802458025080257702473027630	$\Delta(1/4)(\mathrm{ICT})^{f}[\mathrm{cm}^{-1}]$	-	6740	7280	-	7420	-	-
$\Phi'(ICT)$ 00.0220.02500.007700 $\Phi'(ICT)/\Phi(LE)$ 08.82.701.400 $\Phi(ISC)^{g}$ 0.19 ± 0.010.83 ± 0.020.12 ± 0.010.58 ± 0.020.22 ± 0.02 $\Phi(IC)^{h}$ 0.650.150.850.360.77 $\tilde{v}^{max}(S_{1,a}bs) [cm^{-1}]$ 26560288302633027930282702709028840 $\tilde{v}^{max}(S_{2,a}bs) [m^{-1}]^{-1}$ 3430530037903270714028305300 $\tilde{v}^{max}(S_{2,a}bs) [m^{-1}]^{-1}$ 35210335203617033490328303447033540 $\tilde{v}^{max}(S_{2,a}bs) [m^{-1}]^{-1}$ 4260264802458025080257702473027630 $K_{(S_1)}[cm^{-1}]$ 2426026480248025080257702770277027630	$\Phi(LE)$	0.17	0.0025	0.0033	0.061	0.0054	0.20	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Phi'(ICT)$	0	0.022	0.025	0	0.0077	0	0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Phi'(\text{ICT})/\Phi(\text{LE})$	0	8.8	2.7	0	1.4	0	0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Phi(ISC)^g$	0.19 ± 0.01	0.83 ± 0.02	0.12 ± 0.01	0.58 ± 0.02	0.22 ± 0.02		
$\vec{\nu}^{\max}(S_{1,a}bs) [m^{-1}] = 26560 = 28830 = 26330 = 27930 = 28270 = 27090 = 28840 \\ \vec{\nu}^{\max}(S_{1,a}bs) [M^{-1} cm^{-1}] = 3430 = 5300 = 3790 = 3270 = 7140 = 2830 = 5300 \\ \vec{\nu}^{\max}(S_{2,a}bs) [m^{-1}cm^{-1}] = 35210 = 33520 = 36170 = 33490 = 32830 = 34470 = 33540 \\ \vec{\nu}^{\max}(S_{2,a}bs) [M^{-1}cm^{-1}] = 9570 = 24210 = 8170 = 4690 = 25380 = 14310 = 24220 \\ \vec{E}(S_1)^i [cm^{-1}] = 24260 = 26480 = 24580 = 25080 = 25770 = 24730 = 27630 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 4650 = 7780 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 4650 = 7780 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 4650 = 7780 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 4650 = 7780 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 4650 = 7780 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 4650 = 7780 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 25770 = 24730 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 25770 = 24730 = 5770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 25770 = 25770 = 25770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 25770 = 25770 = 25770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 4600 = 9840 = 5560 = 25770 = 25770 = 25770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 2650 = 2650 = 2650 = 25770 = 25770 = 25770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 25770 = 25770 = 25770 = 25770 = 25770 = 25770 = 25770 \\ \vec{E}(S_1)^i [cm^{-1}] = 8650 = 25770 = 25$	$\Phi(\mathrm{IC})^h$	0.65	0.15	0.85	0.36	0.77		
$\varepsilon^{\max}(S_{1,a}bs) [M^{-1} cm^{-1}]$ 3430530037903270714028305300 $\tilde{\nu}^{\max}(S_{2,a}bs) [cm^{-1}]$ 35210335203617033490328303447033540 $\varepsilon^{\max}(S_{2,a}bs) [M^{-1}cm^{-1}]$ 95702421081704690253801431024220 $E(S_1)^i [cm^{-1}]$ 24260264802458025080257702473027630	$\tilde{v}^{\max}(S_1, abs) [cm^{-1}]$	26560	28830	26330	27930	28270	27090	28840
$\tilde{v}^{\max}(S_{2,a}bs) [cm^{-1}]$ 35210 33520 36170 33490 32830 34470 33540 $\varepsilon^{\max}(S_{2,a}bs) [M^{-1}cm^{-1}]$ 9570 24210 8170 4690 25380 14310 24220 $E(S_1)^i [cm^{-1}]$ 24260 26480 24580 25080 25770 24730 27630 $\Delta V(c,S_1)^i [cm^{-1}]$ 9650 4600 5560 5570 5770	$\varepsilon^{\max}(S_1, abs) [M^{-1} cm^{-1}]$	3430	5300	3790	3270	7140	2830	5300
$\varepsilon^{\max}(S_{2,2}abs) [M^{-1}cm^{-1}]$ 9570 24210 8170 4690 25380 14310 24220 $E(S_1)^i [cm^{-1}]$ 24260 26480 24580 25080 25770 24730 27630 $\Delta V(cS_1)^i [cm^{-1}]$ 9650 4600 5560 2570 24730 5700	$\tilde{v}^{\max}(S_{2}$, abs) [cm ⁻¹]	35210	33520	36170	33490	32830	34470	33540
$E(S_1)^i [cm^{-1}]$ 24260 26480 24580 25080 25770 24730 27630	$\varepsilon^{\max}(S_{2}abs) [M^{-1}cm^{-1}]$	9570	24210	8170	4690	25380	14310	24220
$AF(S,S)i[-m^{-1}]$ 9(50 4(00 0940 55(0 4550 7300 5700	$E(S_1)^i [cm^{-1}]$	24260	26480	24580	25080	25770	24730	27630
$\Delta E(5_{10}5_{2})' [cm] = \frac{800}{100} + \frac{400}{100} + \frac{9840}{9840} + \frac{5500}{100} + \frac{4550}{100} - \frac{100}{100} + \frac{100}{100} +$	$\Delta E(S_1,S_2)^j [cm^{-1}]$	8650	4690	9840	5560	4550	7380	5780

^{*a*} Full width at half-maximum (fwhm) of the total fluorescence band. ^{*b*} Fwhm for the separated LE band. ^{*c*} Fwhm for the separated ICT band. ^{*d*} Full width at quarter-maximum (fwqm) of the total fluorescence band. ^{*e*} Fwqm for the separated LE band. ^{*f*} Fwqm for the separated ICT band. ^{*g*} Measurements (at 23 °C) as in refs 26 and 34. ^{*h*} Φ (IC) = 1 – Φ (LE) – Φ '(ICT) – Φ (ISC). ^{*i*} Crossing point of the normalized fluorescence and absorption spectra. ^{*j*} Energy difference $\tilde{\nu}^{max}(S_{2r}abs) - \tilde{\nu}^{max}(S_{1r}abs)$.



Figure 6. Fluorescence (LE+ICT) of (a) 24DCMIA, (b) 25DCMIA, and (c) 34DCMIA in MeCN at -45 °C.

 $\Delta E(S_1,S_2)$ can hence not be reponsible for the increase in $\Phi'(ICT)/\Phi(LE).$

A second consequence of the presence of an isopropyl group in 24- and 34DCMIA, however, is the fact that iPrNMe₂ is a better electron donor than trimethylamine $N(Me)_3$, a model for the donor substituent in the mnDCDMAs. This can be deduced from their vertical ionization energies (vIE): 8.20 eV ($iPrN(Me)_2$) and 8.53 eV $(N(Me)_3)$.⁴¹ Other values of vIE in the literature are 8.00 eV^{42a} for iPrN(Me)₂ and 8.44 eV^{42b} for N(Me)₃, leading to the same conclusion. An oxidation potential of $iPrN(Me)_2$ is not available. Via extrapolation in a plot of vIE vs $E(D/D^+)$ for aliphatic amines (Table S1 and Figure S4 in SI), an oxidation potential of 0.84 V vs SCE could be determined, showing that $iPrN(Me)_2$ is indeed a better donor than $N(Me)_3$ (1.05 V vs SCE).¹⁰ As the calculated energy E(ICT) of the ICT state of the six mnDCDMAs in n-hexane as well as MeCN is already lower than $E(S_1)$,¹⁰ the same will certainly be the case for the mnDCMIAs: E(ICT) is 0.21 eV \simeq 20 kJ/mol lower (difference in $E(D/D^+)$, whereas $E(S_1)$ is only slightly smaller (at most 0.08 eV, Tables 2–5). The absence of an LE \rightarrow ICT reaction with the mnDCDMAs and mnDCMIAs in n-hexane therefore makes clear that E(ICT) can not be calculated employing the redox potentials of the D and A subgroups,¹⁰ which means that the D and A units in the dicyanoanilines are not electronically decoupled.

25DCMIA. Especially for 25DCMIA (9840 cm⁻¹), but also for 23DCMIA (8650 cm⁻¹), the energy gap $\Delta E(S_1,S_2)$ in MeCN is considerably larger than that of 24DCMIA (4690 cm⁻¹) and 34DCMIA (4550 cm⁻¹) but also larger than for 26DCMIA Scheme 1



(5560 cm⁻¹) and 35DCMIA (7380 cm⁻¹), which only show LE emission (Figure 5). Nevertheless, efficient ICT emission with a large $\Phi'(ICT)/\Phi(LE)$ of 2.7 is observed, as mentioned above (Table 5). Similarly, $\Delta E(S_1,S_2)$ is only 270 cm⁻¹ smaller for 25DCMIA than for 25DCDMA (Tables 3 and 5) although an efficient LE \rightarrow ICT reaction is found with 25DCMIA ($\Phi'(ICT)/\Phi(LE) = 2.7$), whereas such a reaction only just starts to appear with 25DCDMA (Figures 5c and 3c).

This observation is a clear indication that the magnitude of $\Delta E(S_1,S_2)$ is not the only criterion which determines whether an LE \rightarrow ICT reaction will take place or not with D/A-substituted benzenes. The appearance of an ICT reaction with 25DCMIA in MeCN will in fact be due to the large amino twist angle $\theta = 42.6^{\circ}$ of 25DCMIA (Table 1). Such a large twist angle leads to an efficient electronic decoupling between the amino and benzonitrile moieties. Under these conditions, the ICT state becomes similar to a weakly coupled intermolecular exciplex ${}^{1}(A^{-}D^{+})$, as with DTABN, 30 mDTABN, 30 MMD, 31 6-cyanobenzoquinuclidine (CBQ), 11,13,39 and also CVL. 36 Evidently, the magnitude of $\Delta E(S_1,S_2)$ does not govern the occurrence of an ICT reaction in these D/A molecules with electronically decoupled D and A subunits, different from DMABN and its strongly coupled derivatives.⁷

Intersystem Crossing and Internal Conversion. With the mnDCDMAs as well as the mnDCMIAs, ISC and IC are important deactivation channels at 25 °C (Tables 2–5).^{15,34,37} In *n*-hexane, $\Phi(ISC)$ of the mnDCDMAs ranges between 0.45 and 0.81 and between 0.56 and 0.85 for the mnDCMIAs, with $\Phi(IC)$ between 0.12 and 0.46 (mnDCDMA) and between 0.09 and 0.28 (mnDCMIAs). In MeCN, $\Phi(ISC)$ of the mnDCDMAs lies between 0.08 and 0.90 and between 0.12 and 0.83 for the mnDCMIAs, with $\Phi(IC)$ between 0.15 and 0.85 (mnDCMIAs). Note that in *n*-hexane ISC and IC originate from S₁(LE), whereas with 24DCDMA, 34DCDMA, 24DCMIA, 34DCMIA, and 25DCMIA in MeCN these deactivation processes start from the LE as well as the ICT state.

Φ'(ICT)/Φ(LE) as a Function of Temperature. Stevens–Ban Plots. For systems with two kinetically interconverting states, such as LE and ICT in Scheme 1, the ratio Φ'(ICT)/Φ(LE) can be expressed by the following equation.^{7,24,34,40,43,44}

$$\Phi'(\text{ICT})/\Phi(\text{LE}) = k_{\text{f}}'(\text{ICT})/k_{\text{f}}(\text{LE})\{k_{\text{a}}/(k_{\text{d}} + 1/\tau_{\text{o}}'(\text{ICT}))\}$$
(1)

When $k_d \gg 1/\tau'_o$ (ICT), with a small ICT reaction enthalpy difference $-\Delta H$,⁴⁴ eq 1 simplifies the high-temperature limit (HTL) to eq 2.

$$\Phi'(\text{ICT})/\Phi(\text{LE}) = k_{\text{f}}'(\text{ICT})/k_{\text{f}}(\text{LE})k_{\text{a}}/k_{\text{d}}$$
(2)

Alternatively, when $k_d \ll 1/\tau'_o(\text{ICT})$, the low-temperature limit (LTL) (large $-\Delta H$),⁷ eq 3, holds.

$$\Phi'(\text{ICT})/\Phi(\text{LE}) = (k'_{\text{f}}(\text{ICT})/k_{\text{f}}(\text{LE}))k_{\text{a}}\tau'_{\text{o}}(\text{ICT})$$
(3)

In eqs 1–3 and Scheme 1, k_a and k_d are the rate constants of the forward and backward ICT reaction; $\tau_0(LE)$ is the fluorescence



Figure 7. Stevens—Ban (SB) plots of $\Phi'(\text{ICT})/\Phi(\text{LE})$ vs 1000/T in MeCN of (a) 24DCDMA, (b) 24DCMIA, and (c) 34DCMIA. The ICT reaction enthalpies ΔH of the LE \rightarrow ICT reaction are indicated in the figures.

Table 6. ICT Stabilization Enthalpy Difference $-\Delta H(SB)$ and ICT/LE Fluorescence Quantum Yield Ratio $\Phi'(ICT)/\Phi(LE)$ at 25 °C for 24DCDMA, 24DCMIA, and 34DCMIA in MeCN

D/A molecule	$-\Delta H(SB)$ (kJ/mol)	$\Phi'(\text{ICT})/\Phi(\text{LE})$
24DCDMA	5.4	1.2^a
24DCMIA	4.7	8.8^b
34DCMIA	3.9	1.4^b
^{<i>a</i>} Table 3. ^{<i>b</i>} Table 5.		

lifetime of the model compound (no ICT); $\tau'_0(ICT)$ is the fluorescence lifetime of the ICT state; and $k_f(LE)$ and $k'_f(ICT)$

able 7. LE or ICI	Huo	rescen	ce Maxim	a $\tilde{v}^{\max}(\mathbf{I}($	CT) of the mnl	OCDMAs and DI	ABN at 25 °C	in a Series of	Solvents			
solvent	ట	2	$f(\varepsilon)$ - 1/2 $f(n^2)$	$f(\varepsilon)$ - $f(n^2)$ [:	23DCDMA 1000 cm ⁻¹] LE [1	24DCDMA 000 cm ⁻¹] LE/ICT	25DCDMA [1000 cm ⁻¹] LE	26DCDMA [1000 cm ⁻¹] LE	34DCDMA [1000 cm ⁻¹] LE/ICT	35DCDMA [1000 cm ⁻¹] LE	24DCP4C [1000 cm ⁻¹] LE	DIABN ^a 1000 cm ⁻¹] ICT
n-hexane (1)	1.88	1.372	0.092	0.000	24.41	26.37/ -	24.34	25.18	26.47/ -	25.91	26.57	25.72
di-n-butyl	3.05	1.397	0.192	0.095	23.27	25.46/ -	23.20	24.43	25.24/ -	24.72		24.30
ether (2)												
diethyl ether (3)	4.24	1.350	0.253	0.165	22.92	25.18/ -	22.86	24.21	24.85/21.76	24.32	25.69	23.52
ethyl acetate (4)	5.99	1.370	0.292	0.200	,	1	ı	ı	23.84/20.32	23.20		22.26
methyl	6.88	1.358	0.308	0.218	21.70	24.35/20.34	21.55	23.35	23.72/20.21	23.10		21.96
acetate (5)												
tetrahydrofuran (6)	7.39	1.405	0.307	0.208	21.87	24.43/20.61	21.72	23.44	23.84/20.16	23.23	25.08	22.38
1,2-dichloroethane (7)	10.4	1.443	0.326	0.221	22.17	24.74/21.23	22.18	23.98	23.99/20.50	23.65		21.65
<i>n</i> -propyl cyanide (8)	24.2	1.382	0.375	0.281	21.50	24.24/20.10	21.40	23.41	23.36/19.49	22.81		21.09
ethyl cyanide (9)	29.2	1.363	0.384	0.293	21.35	24.10/19.84	21.29	23.31	23.26/19.42	22.67	24.88	20.87
acetonitrile (10)	36.7	1.342	0.393	0.306	21.18	23.88/19.40	21.07	23.17	23.04/19.16	22.51	24.82	20.49

Table 8.	Data from	the Solvatoc	hromic Analysis	of the LI	or ICT F	luorescence N	Λ axima $\tilde{\nu}^{\max}$	of the mn D)CDMAs
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D/A molecule	$ ho^{a}$ [Å]	$\mu_{g}^{a}[D]$	slope (LE)	$\mu_{\rm e}({\rm LE})^a$ [D]	slope (ICT)	$\mu_{\rm e}({\rm ICT})^a [{\rm D}]$
23DCDMA (eq 4)	4.43	7.5	-10480 ± 800	14.0 ± 0.4		
23DCDMA (vs DIABN)	4.43 (4.68)	7.5 (6.8)	1.13 ± 0.03	$14.5 \pm 0.4 (18)$		
23DCDMA (vs DMABN)	4.43 (4.20)	7.5 (6.6)	1.73 ± 0.11	$12.8\pm 0.3(10)$		
24DCDMA (eq 4)	4.43	5.1	-7760 ± 650	11.1 ± 0.4	-12360 ± 5120	13.2 ± 2.1
24DCDMA (vs DIABN)	4.43 (4.68)	5.1 (6.8)	0.44 ± 0.04	$11.6 \pm 0.4 (18)$	0.66 ± 0.30	$13.5 \pm 2.4 (18)$
24DCDMA (vs DMABN)	4.43 (4.20)	5.1 (6.6)	1.20 ± 0.08	$10.2 \pm 0.4 (10)$	0.56 ± 0.10	$13.7\pm 0.9(17)$
25DCDMA (eq 4)	4.43	1.4	-10600 ± 950	10.3 ± 0.5		
25DCDMA (vs DIABN)	4.43 (4.68)	1.4 (6.8)	0.61 ± 0.07	$10.9 \pm 0.6 (18)$		
25DCDMA (vs DMABN)	4.43 (4.20)	1.4 (6.6)	1.76 ± 0.10	$9.1\pm 0.3(10)$		
26DCDMA (eq 4)	4.43	3.3	-6350 ± 850	9.3 ± 0.5		
26DCDMA (vs DIABN)	4.43 (4.68)	3.3 (6.8)	0.37 ± 0.04	$9.8\pm 0.5(18)$		
26DCDMA (vs DMABN)	4.43 (4.20)	3.3 (6.6)	1.08 ± 0.10	$8.4 \pm 0.3 (10)$		
34DCDMA (eq 4)	4.43	7.8	-11060 ± 750	14.4 ± 0.4	-15350 ± 2500	16.1 ± 0.9
34DCDMA (vs DIABN)	4.43 (4.68)	7.8 (6.8)	0.63 ± 0.04	$15.0 \pm 0.4 (18)$	0.79 ± 0.20	$16.2\pm 0.9(18)$
34DCDMA (vs DMABN)	4.43 (4.20)	7.8 (6.6)	1.82 ± 0.10	$13.3\pm0.3(10)$	0.73 ± 0.10	$16.8\pm 0.4(17)$
35DCDMA (eq 4)	4.43	5.2	-11080 ± 950	12.7 ± 0.4		
35DCDMA (vs DIABN)	4.43 (4.68)	5.2 (6.8)	0.63 ± 0.06	$13.3\pm 0.5(18)$		
35DCDMA (vs DMABN)	4.43 (4.20)	5.2 (6.6)	1.83 ± 0.10	$11.6 \pm 0.3 (10)$		
24DCP4C (eq 4)	4.53	5.9	-5840 ± 650	10.9 ± 0.4		
24DCP4C (vs DIABN)	4.53 (4.68)	5.9 (6.8)	0.94 ± 0.03	$9.9 \pm 0.1 (18)$		
24DCP4C (vs DMABN)	4.53 (4.20)	5.9 (6.6)	0.34 ± 0.04	$11.3\pm 0.5(10)$		
			. 1. 1	1 1 11 11 11 10 (2)	1. 1 11 1.	

^{*a*} Values in parentheses are for DIABN or DMABN. Ground state dipole moment μ_g calculated by PM3; results obtained by scaling via a comparison of the calculated μ_g (DMABN) = 5.94 D (PM3) and its experimental value of 6.6 D (refs 4 and 52).

are the radiative rate constants. The reciprocal of these lifetimes is equal to the sum of their radiative and nonradiative rate constants.

In Figure 7, Stevens–Ban (SB)⁷ plots, $\ln(\Phi'(ICT)/\Phi(LE))$ vs 1000/*T*, are presented for (a) 24DCDMA, (b) 24DCMIA, and (c) 34DCMIA in MeCN. $\Phi'(ICT)/\Phi(LE)$ increases upon cooling, which means that the systems are in the HTL condition (eq 2), with $k_d \gg 1/\tau'_0(ICT)$, which appears with relatively small $-\Delta H$ values,⁴ such as the -H(SB)s determined here (Table 6): 5.4 kJ/mol (24DCDMA), 4.7 kJ/mol (24DCMIA), and 3.9 kJ/mol (34DCMIA). For DMABN in MeCN, by comparison, $-\Delta H = 27.0 \text{ kJ/mol}$,⁷ whereas for DMABN in toluene (HTL),^{43,4} $-\Delta H = 11.6 \text{ kJ/mol}$.

Solvatochromic Measurements. Excited State Dipole Moments $\mu_{e}(LE)$ and $\mu_{e}(ICT)$. For the six mnDCDMAs and mnDCMIAs, the maxima $\tilde{\nu}^{max}(LE)$ and $\tilde{\nu}^{max}(ICT)$ of the LE and ICT fluorescence bands of these compounds were measured in a series of solvents, from the nonpolar *n*-hexane ($\varepsilon^{25} = 1.88$) to the strongly polar MeCN ($\varepsilon^{25} = 36.7$), see Table 7. From these data, $\mu_{e}(ICT)$ can be determined from the slope of a plot of $\tilde{\nu}^{max}(ICT)$ vs the solvent polarity parameter $g(\varepsilon,n) = f(\varepsilon) - 1/2f(n^2)$, whereas $\mu_{e}(LE)$ can be obtained from the slope of the plot of $\tilde{\nu}^{max}(LE)$ vs the solvent polarity parameter $g(\varepsilon,n) = f(\varepsilon) - f(n^2)$ (eqs 4-6).^{26,40,44-49} This difference in $g(\varepsilon,n)$ appears while the ICT state is not directly populated by absorption in S₀ but is formed from the initially excited LE precursor (see below).^{26,40,46}

$$v^{\text{max}}(\text{flu}) = -\frac{1}{2hc\rho^3}\mu_e(\mu_e - \mu_g)g(\varepsilon, n) + \text{const.}$$
 (4)

$$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1} \tag{5}$$

$$f(n^2) = \frac{n^2 - 1}{2n^2 + 1} \tag{6}$$

In eqs 4–6, $\mu_{\rm g}$ and $\mu_{\rm e}$ are the ground and excited state dipole moments; ε is the dielectric constant; *n* is the refractive index; *h* is Planck's constant; *c* is the speed of light; and ρ is the Onsager radius^{46,52} of the solute.

Six mnDCDMAs. The fluorescence maxima $\tilde{\nu}^{max}(LE)$ and $\tilde{\nu}^{max}(ICT)$ of the six mnDCDMAs in a series of solvents at 25 °C (Table 7) are plotted vs the $\tilde{\nu}^{max}(ICT)$ of DIABN in Figure S5a,c,e,g,i,h (SI) and also against the solvent polarity parameter $g(\varepsilon,n)$ (eqs 4–6) in Figure S5b,d,f,h,j,l (SI). The LE and ICT emission maxima are, as usual, ^{15,44,50} also plotted against the $\tilde{\nu}^{max}(ICT)$ of DIABN($\mu_e(ICT) = 18$ D).⁵¹ With this procedure, the scatter in the data points is generally reduced by mutually compensating the specific solute/solvent interactions.^{26,40,48,51}

For the four mnDCDMAs, 23DCDMA, 25DCDMA, 26DCDMA, and 35DCDMA, which only show a single LE fluorescence in *n*-hexane and MeCN (Figures 2a,c,d,f and 3a,c, d,f), the following dipole moments $\mu_{e}(LE)$ are calculated, taking the mean value of the results from the plots of $\tilde{v}^{max}(LE)$ vs $\tilde{v}^{max}(ICT,DIABN)$ and $g(\varepsilon,n) = f(\varepsilon) - f(n^2)$ (eqs 4–6): 14 D (23DCDMA), 11 D (25DCDMA), 10 D (26DCDMA), and 13 D (35DCDMA) (see Table 8).

For the two DCDMAs showing dual LE + ICT fluorescence in MeCN (Figure 3b,e), the averaged $\mu_e(LE)$ values are 11 D (24DCDMA) and 15 D (34DCDMA), whereas from the plots of $\tilde{v}^{\max}(ICT)$ vs $g(\varepsilon,n) = f(\varepsilon) - 1/2f(n^2)$ somewhat larger dipole moments $\mu_e(ICT)$ are found: 13 D for 24DCDMA and 16 D for 34DCDMA (Table 8). The increase in dipole moment when going from LE to ICT is for 24DCDMA and 34DCDMA smaller than that observed for

Table 9. LE or ICI	Fluor	escence	e Maxima $\widetilde{v}^{_1}$	max(ICT) of mnDCMIA	and DIABN at 25	°C in a Series of So	lvents			
solvent	ω	и	$f(arepsilon) = -1/2 f(n^2)$	$f(\varepsilon) - f(n^2)$	23DCMIA [1000 cm ⁻¹] LE	24DCMIA [1000 cm ⁻¹] LE/ICT	25DCMIA [1000 cm ⁻¹] LE/ICT	26DCMIA [1000 cm ⁻¹] LE	34DCMIA [1000 cm ⁻¹] LE/ICT	35DCMIA [1000 cm ⁻¹] LE	DIABN [1000 cm ⁻¹] ICT
<i>n</i> -hexane (1)	1.88	1.372	0.092	0.000	23.91	25.63/ -	23.73/ -	24.64	25.94/ -	25.30	25.72
di-n-propyl ether (2)	3.26	1.379	0.207	0.113	23.00	24.90/21.95	22.92/21.39	23.93	24.83/ -	24.29	24.09
diethyl ether (3)	4.24	1.350	0.253	0.165	22.74	24.57/21.61	22.67/20.83	23.70	24.55/19.97	24.04	23.52
ethyl acetate (4)	5.99	1.370	0.292	0.200	21.64	24.26/20.19	21.91/20.78	23.19	23.54/19.03	22.98	22.26
tetrahydrofuran (5)	7.39	1.405	0.307	0.208	21.71	,	22.09/20.47	23.27	23.60/19.20	23.06	22.38
1,2-dichloroethane (6)	10.4	1.443	0.326	0.221	21.77	24.18/20.79	22.12/20.77	23.68	23.46/19.17	23.17	21.65
<i>n</i> -propyl cyanide (7)	24.2	1.382	0.375	0.281		,	22.13/20.04	ı	22.89/17.92	ı	21.09
ethyl cyanide (8)	29.2	1.363	0.384	0.293	21.12	23.64/19.53	22.16/19.52	22.61	22.71/17.67	22.50	20.87
acetonitrile (9)	36.7	1.342	0.393	0.306	21.03	23.62/19.43	22.06/19.22	22.52	22.51/17.28	22.32	20.49

DMABN, for which $\mu_e(LE) = 10 \text{ D}$ and $\mu_e(ICT) = 17 \text{ D}.^{52}$ The reason for this perhaps unexpected difference may

find its origin in possibly different dipole moment directions of the LE and ICT states in the dicyano-substituted compounds.⁵³ This small difference between $\mu_{e}(LE)$ and $\mu_{e}(ICT)$ for 24DCDMA and 34DCDMA also shows that not the absolute magnitude of a dipole moment determines whether its origin is an LE or an ICT state, as stressed in our definition of an LE and ICT states in ref 1. For DMABN in *n*-hexane (no ICT emission), $\mu_{\rm e}(\rm LE)$ is already relatively large (10 D), which does not mean that it is the dipole moment of an ICT state.

Comparison with Calculations. From computations¹⁸ with 34DCDMA (gas phase), the following results are obtained: $\mu_{\sigma}(S_0)$ = 10.7 D, $\mu_{e}(S_{1}, TICT) = 23.7$ D, and $\mu_{e}(S_{2}, LE) = 21.2$ D. It should be noted, as mentioned in the Introduction, that the lowest excited and hence emitting state is considered to be a TICT state, without the occurrence of dual fluorescence,¹⁸ different from our observation. These calculated dipole moment data are substantially larger than our results (Table 8): $\mu_{\alpha}(S_0) = 7.8 \text{ D} (\text{PM3}), \mu_{e}(S_1,\text{LE}) = 15 \text{ D}$ (vs DIABN), and $\mu_{e}(ICT) = 16$ D. The computations¹⁸ with 35DCDMA (gas phase, only LE) also result in larger dipole moments than those obtained from our investigations: $\mu_g(S_0) = 7.5$, $\mu_e(S_1,CT)$ = 19.4 D, and $\mu_e(S_2, LE)$ = 19.4 D (ref 18) as compared with $\mu_e(S_0)$ = 5.2 D (PM3) and $\mu_{e}(LE) = 13$ D (vs DIABN) (see Table 8). The difference between the calculated and experimental dipole moments $\mu_{\rm e}({\rm ICT})$ and $\mu_{\rm e}({\rm LE})$ could indicate that the most stable molecular structure obtained in the computations is not the one encountered in our experiments. For a similar conclusion in the case of DMABN, see ref 21.

Six mnDCMIAs. For the six mnDCMIAs (Table 9), the solvatochromic plots vs $\tilde{v}^{\max}(\text{ICT,DIABN})$ and $g(\varepsilon,n)$ are presented in Figures S6a,c,e,g,i,k and S61b,d,f,h,j,l (SI) (eqs 4-6). The averaged dipole moments $\mu_{e}(LE)$ (Table 10) are: 15 D (23DCMIA), 12 D (24DCMIA), 9 D (25DCMIA), 10 D (26DCMIA), 16 D (34DCMIA), and 13 D (35DCMIA). These LE dipole moments are comparable with those obtained for the corresponding mnDCDMAs (Table 8). The ICT dipole moments $\mu_{e}(ICT)$ of the three mnDCMIAs for which a separation of the overall fluorescence spectrum in an LE and ICT contribution could be made (Figure 5b,c,e), are again somewhat larger than their LE dipole moments: 15 D for 24DCMIA, 11 D for 25DCMIA, and 18 D for 34DCMIA (Table 10).

24DCP4C. The dipole moment of 24DCP4C has an average value of 11 D ($\mu_e(LE)$, Table 8), supporting the identification of its fluorescence as a single LE emission, as discussed above.

LE Fluorescence Decays with the mnDCDMAs and mnDCMIAs. Literature Data. Picosecond fluorescence decays, with a time resolution of 5 ps, have appeared in the literature for 35DCDMA in MeCN and diethyl ether (DEE) as well as for 34DCDMA in DEE. These decays are single exponential, with times au_1 in the nanosecond domain, without any indication of a second, shorter picosecond decay time.^{9,11} For 35DCDMA, τ_1 equals 18.8 ns in MeCN⁹ at 25 °C and 16.9 ns in DEE¹¹ at -89 °C, whereas for 34DCDMA in DEE¹¹ τ_1 is 6.88 ns at 25 °C and 10.2 ns at -100 °C. In view of their single exponential character, these decays were attributed to LE. It was then concluded that an ICT reaction does not take place under the experimental conditions, caused by the relatively large energy gap $\Delta \dot{E}(S_1,S_2)$ of 35DCDMA and 34DCDMA, as discussed above.^{9,11–14}

Nanosecond Fluorescence Decays of mnDCDMAs and mnDCMIAs Without ICT Emission. n-Hexane and MeCN. The LE fluorescence decays of all mnDCDMAs and mnDCMIAs

Table 10. Data	a from the Solva	tochromic Analysis.	s of the LE or	ICT Fluorescence	Maxima \tilde{v}^{\max} of	f the mnDCMIAs
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D/A molecule	$ ho^a$ [Å]	$\mu_{g}^{a}[D]$	slope (LE)	$\mu_{\rm e}({\rm LE})^a$ [D]	slope (ICT)	$\mu_{\rm e}({\rm ICT})^a [{\rm D}]$
23DCMIA (eq 4)	4.66	7.5	-9920 ± 950	14.4 ± 0.5		
23DCMIA (vs DIABN)	4.66 (4.68)	7.5 (6.8)	0.57 ± 0.04	$15.0\pm 0.4(18)$		
23DCMIA (vs DMABN)	4.66 (4.20)	7.5 (6.6)	1.56 ± 0.12	$13.0 \pm 0.4 (10)$		
24DCMIA (eq 4)	4.66	6.1	-6700 ± 150	11.8 ± 0.1	-13520 ± 2500	15.1 ± 1.0
24DCMIA (vs DIABN)	4.66 (4.68)	6.1 (6.8)	0.378 ± 0.02	$12.2\pm 0.3(18)$	0.69 ± 0.12	$15.2 \pm 1.0 (18)$
24DCMIA (vs DMABN)	4.66 (4.20)	6.1 (6.6)	1.06 ± 0.08	$10.7 \pm 0.3 (10)$	0.60 ± 0.04	$15.4 \pm 0.4 (17)$
25DCMIA (eq 4)	4.66	2.5	-5390 ± 1020	8.7 ± 0.7	-10230 ± 1740	11.5 ± 0.9
25DCMIA (vs DIABN)	4.66 (4.68)	2.5 (6.8)	0.31 ± 0.07	$9.2 \pm 0.8 (18)$	0.51 ± 0.11	$11.4 \pm 1.0 (18)$
25DCMIA (vs DMABN)	4.43 (4.20)	2.5 (6.6)	0.91 ± 0.10	$7.9 \pm 0.4 (10)$	0.43 ± 0.08	$11.5 \pm 0.9 (17)$
26DCMIA (eq 4)	4.66	2.8	-6800 ± 900	9.8 ± 0.5		
26DCMIA (vs DIABN)	4.66 (4.68)	2.8 (6.8)	0.38 ± 0.06	$10.2 \pm 0.7 (18)$		
26DCMIA (vs DMABN)	4.66 (4.20)	2.8 (6.6)	1.07 ± 0.13	$8.6 \pm 0.4 (10)$		
34DCDMA (eq 4)	4.66	8.2	-11410 ± 700	15.5 ± 0.3	-18010 ± 2130	18.2 ± 0.8
34DCMIA (vs DIABN)	4.66 (4.68)	8.2 (6.8)	0.65 ± 0.02	$16.2 \pm 0.2 (18)$	0.89 ± 0.15	$18.0 \pm 1.0(18)$
34DCMIA (vs DMABN)	4.66 (4.20)	8.2 (6.6)	1.79 ± 0.16	$14.1 \pm 0.4 (10)$	0.79 ± 0.10	$18.5\pm 0.8(17)$
35DCMIA (eq 4)	4.66	5.5	-9980 ± 900	13.1 ± 0.5		
35DCMIA (vs DIABN)	4.66 (4.68)	5.5 (6.8)	0.57 ± 0.04	$13.7 \pm 0.4 (18)$		
35DCMIA (vs DMABN)	4.66 (4.20)	5.5 (6.6)	1.57 ± 0.12	$11.7\pm 0.3(10)$		
^a Values in parentheses are fo	r DIABN or DMA	ABN. Ground sta	ate dipole moment μ_{g} c	alculated by PM3; resi	ults obtained by scaling	via a comparison o

^{*a*} Values in parentheses are for DIABN or DMABN. Ground state dipole moment μ_g calculated by PM3; results obtained by scaling via a comparison of the calculated μ_g (DMABN) = 5.94 D (PM3) and its experimental value of 6.6 D (refs 4 and 52).

in *n*-hexane at 25 °C are single exponential, with times τ_1 in the nanosecond time range, between 0.82 ns (26DCDMA) and 9.77 ns (25DCMIA) (Tables 11 and 12). In MeCN at 25 °C, single exponential nanosecond decays are likewise observed with the dicyanoanilines for which dual LE + ICT fluorescence could not be detected with certainty: 23DCDMA, 25DCDMA, 26DCDMA, and 35DCDMA (Figure 3a,c,d,f) as well as 23DCMIA, 26DCMIA, and 35DCMIA (Figure 5a,d,f) (see Tables 11 and 12). These results support our conclusion based on the absence of an ICT emission (see Figures 2−5) that an LE → ICT reaction does not take place with these molecules. k'_f (ICT) is smaller than k_f (LE) (Tables 11 and 12), as generally observed,^{4,6,7,30,34,43} because of the larger CT character of the ICT as compared with the LE state.¹⁴

Double Exponential LE and ICT Picosecond Decays. 24DCDMA, 24DCMIA, 34DCMIA, and 25DCMIA. The picosecond fluorescence decays of 24DCDMA, 24DCMIA, and 34DCMIA in MeCN at 25 °C (Figures 8–10), which undergo an ICT reaction and show dual LE + ICT fluorescence (Figures 3b and 5b,c,e), can not adequately be fitted with a single exponential. The LE and ICT fluorescence decays in MeCN of 24DCDMA are shown in Figure 8 (25 °C), of 24DCMIA in Figure 9 (25 °C), and of 34DCMIA in Figure 10 (25 and -45 °C). Also for 25DCMIA in THF, *n*-propylcyanide (PrCN), and MeCN at lower temperatures (Figure 11), double exponential LE and ICT fluorescence decays are observed, supporting our conclusion discussed above that its fluorescence spectrum consists of overlapping LE and ICT bands (Figure 5c).

24DCDMA in MeCN at 25 °C. The LE and ICT picosecond fluorescence decays of 24DCDMA in MeCN at 25 °C are shown in Figure 8. From a global analysis, two times are obtained: $\tau_2 =$ 1.8 ps and $\tau_1 =$ 3800 ps (eqs 7–9). The shortest time τ_2 (taken from femtosecond transient spectra, see Figures 14 and S7 (SI) below) is kept fixed. The minor additional decay time of 153 ps is attributed to photoproducts, other impurities, or experimental problems and is hence not taken into account in the data analysis (as done before).^{40,55} The ICT fluorescence response function

shows a growing-in (Figure 8b, $A_{22} = -1.8$, eq 8). For 34DCDMA in DEE at -110 °C (Table 13), the LE and ICT decays are double exponential. The ICT reaction is made possible by the strong increase in solvent polarity upon cooling, from $\varepsilon^{25} = 4.24$ to $\varepsilon^{-110} = 9.79$.

$$i_{\rm f}({\rm LE}) = A_{11} \exp(-t/\tau_1) + A_{12} \exp(-t/\tau_2)$$
 (7)

$$i_{\rm f}({\rm ICT}) = A_{21} \exp(-t/\tau_1) + A_{22} \exp(-t/\tau_2)$$

with $A_{22} = -A_{21}$ (8)

$$A = A_{12}/A_{11} \tag{9}$$

As $\tau_2 \ll \tau_1$, the amplitude ratio $A = A_{12}/A_{11}$ (eq 9) of the LE decay (Figure 8a) is approximately equal to the ratio of the forward and backward ICT rate constants k_a/k_d (Scheme 1).^{7,34} In such a case, also $1/\tau_2 \approx (k_a + k_d)$.^{7,34} From the data in Figure 8a, $\tau_2 = 1.8$ ps and A = 7.58, the rate constants $k_a = 49 \times 10^{10}$ s⁻¹ and $k_d = 6.5 \times 10^{10}$ s⁻¹ are then calculated (Table 13).

These results show that not only the LE \rightarrow ICT forward reaction of 24DCDMA in MeCN at 25 °C is very fast, but that this also is the case for the ICT \rightarrow LE back reaction, a clear indication that $-\Delta H$ is relatively small, in accordance with $-\Delta H(SB) = 5.4$ kJ/mol (Table 6). The connection between k_d and $-\Delta H$ is illustrated by the following data. For NTC6 in *n*-hexane at 25 °C, with a very small $-\Delta H$ of 2.4 kJ/mol, $k_d = 32.2 \times 10^{10} \text{ s}^{-1.24}$ With DMABN in MeCN at 25 °C, for comparison, k_d (0.047 $\times 10^{10} \text{ s}^{-1}$) is nearly 140 times smaller than for 24DCDMA (6.5 $\times 10^{10} \text{ s}^{-1}$), due to a much a larger $-\Delta H = 27.0$ kJ/mol than the 5.4 kJ/mol for 24DCDMA (Table 6).⁷

24DCMIA in MeCN at 25 °**C.** The LE and ICT picosecond fluorescence decays of 24DCMIA in MeCN at 25 °C are shown in Figure 9. From the LE decay (Figure 9a), the times $\tau_2 = 3.0$ ps and $\tau_1 = 5460$ ps are obtained, with an amplitude ratio $A_{12}/A_{11} = 24.4$ (Table 13). From these data (see preceding section), $k_a = 32 \times 10^{10} \text{ s}^{-1}$ and $k_d = 1.3 \times 10^{10} \text{ s}^{-1}$ are calculated. For 24DCMIA, k_d

Table 11. Fluorescence Quantum Yields $\Phi(\text{flu})$, Nanosecond Decay Times τ_1 , and Radiative Rate Constants $k_{\rm f}$ for the Six mnDCDMAs in *n*-Hexane, DEE, and MeCN at 25 °C

				$k_{\rm f}({\rm LE})^c$ or $k'_{\rm f}({\rm ICT})^c$
mnDCDMA	solvent	$\Phi({ m flu})^a$	$ au_1^{\ b} \ [\mathrm{ns}]$	$[10^7 \text{ s}^{-1}]$
23DCDMA	<i>n</i> -hexane	0.13	3.27	4.0 (LE)
	DEE	0.33		
	MeCN	0.28	13.3	2.1 (LE)
24DCDMA	<i>n</i> -hexane	0.065	1.45	4.5 (LE)
	DEE	0.077	3.15	2.4 (LE)
	MeCN	0.013 (LE)	$3.80^{d,e}$	0.34 (LE)
		0.016 (ICT)	$3.80^{d,e}$	$0.42^{cf},(ICT)$
25DCDMA	<i>n</i> -hexane	0.31	8.31	3.7 (LE)
	DEE	0.45		
	MeCN	0.046	2.90	1.6 (LE)
26DCDMA	<i>n</i> -hexane	0.066	0.82	8.0 (LE)
	DEE	0.055		
	MeCN	0.096	3.07	3.1 (LE)
34DCDMA	<i>n</i> -hexane	0.17	3.15	5.4 (LE)
	DEE	0.34	6.84 ^{<i>d</i>}	4.9 (LE)
	MeCN	0.022 (LE)	1.10^{d}	2.0 (LE)
		0.0077 (ICT)	1.10^{d}	0.70° (ICT)
35DCDMA	<i>n</i> -hexane	0.095	3.08	3.1 (LE)
	DEE	0.21		
	MeCN	0.16	18.6	0.86 (LE)

^{*a*} LE fluorescence quantum yield $\Phi(LE)$, unless otherwise indicated. Data for *n*-hexane are from Table 2 and those for MeCN from Table 3. ^{*b*} From nanosecond fluorescence decays, with a time resolution better than 0.5 ns (ref 54). For the picosecond decays of 24DCDMA and 34DCDMA in MeCN, see footnote d. ^{*c*} Radiative rate constant: $k_f = \Phi(flu)/\tau_1$. In the case of the dual fluorescent molecules 24DCDMA and 34DCDMA in MeCN, only approximate values are listed for $k_f(LE)$ and $k'_f(ICT)$, as the expressions for these rate constants are more complex (ref 34). See footnote e. ^{*d*} Time resolution ≈ 3 ps (ref 7). ^{*c*} See Figure 8. ^{*f*} The ICT lifetime $\tau'_o(ICT) = 3.44$ ns (Table 13), hence $k'_f(ICT) = \Phi'(ICT)/\tau'_o(ICT) = 0.47 \times 10^7 \text{ s}^{-1}$.

is smaller than for 24DCDMA ($k_d = 6.5 \times 10^{10} \text{ s}^{-1}$, Table 13). Replacing a dimethylamino substituent by isopropylmethylamino results in a larger ICT efficiency, i.e., in a larger $-\Delta H$, such as with the pair DMABN and IMABN (see above).⁴⁰ This is, however, not the case for 24DCDMA and 24DCMIA, having about the same $-\Delta H(\text{SB})$: 5.4 and 4.7 kJ/mol (Table 6). Nevertheless, a larger $\Phi'(\text{ICT})/\Phi(\text{LE})$ of 8.8 is observed for 24DCMIA than for 24DCDMA (1.2); see Tables 3 and 5. The ICT decay of 24DCMIA can in fact be fitted with a single exponential: $\tau_1 = 5120$ ps (Figure 9b,c). The short time $\tau_2 = 3.0$ ps only has a fractional contribution of 3/5460 = 0.055% (for equal amplitudes $-A_{22}$ and A_{21} , eq 8) to the overall ICT fluorescence response function.

24DCMIA in DEE at 25, -**45**, and -**115** °C. From the LE and ICT fluorescence decays of 24DCMIA in DEE at 25 °C (Table 13), the decay times $\tau_2 = 3.4$ ps and $\tau_1 = 5250$ ps, with $A_{12}/A_{11} = 5.9$ (eqs 7–9), are determined by global analysis. These data result in $k_a = 25 \times 10^{10} \text{ s}^{-1}$ and $k_d = 4.3 \times 10^{10} \text{ s}^{-1}$. For 24DCMIA in MeCN at 25 °C (Table 13), k_d is smaller (1.3 × 10¹⁰ s⁻¹), due to the fact that the stabilization of the ICT state ($-\Delta H$) will be larger in the polar MeCN ($\varepsilon^{25} = 36.7$) than in DEE ($\varepsilon^{25} = 4.24$).^{7,44,56}

The LE decay time τ_2 of 24DCMIA in DEE becomes longer when the temperature is lowered, from 3.4 ps (25 °C), via 4.8 ps

(-45 °C), to 21.8 ps (-115 °C), whereas the corresponding amplitude ratio A_{12}/A_{11} increases: 5.9, 24.9, and 75.2 (Table 13). This means that the ratio $k_a/k_d \ (\approx A_{12}/A_{11})^7$ also increases, because k_d decreases stronger than k_a , as the activation barrier E_d is larger than E_a , which is always the case when a molecule undergoes an ICT reaction, i.e., when $\Delta H \ (= E_a - E_d)$ is negative.^{4,7,34,43,44,56–58} Note that ΔH for DEE is not a constant, as its polarity and hence $-\Delta H$ increase upon cooling, from $\varepsilon^{25} = 4.24$ to $\varepsilon^{-115} = 11.55$.

34DCMIA in MeCN at 25 and -45 °C. A global analysis of the LE and ICT picosecond fluorescence decays of 34DCMIA in MeCN at 25 °C is presented in Figure 10a, with a growing-in (negative A_{22} , eq 8) for the ICT fluorescence response function. From the times $\tau_2 = 4.6$ ps and $\tau_1 = 1360$ ps, together with $A_{12}/A_{11} = 5.5$, $k_a = 18 \times 10^{10}$ s⁻¹ and $k_d = 3.3 \times 10^{10}$ s⁻¹ are obtained (Table 13). Both rate constants become smaller upon cooling, to be expected for activated processes. At -45 °C, $k_a = 14 \times 10^{10}$ s⁻¹ and $k_d = 0.76 \times 10^{10}$ s⁻¹ (Table 13), calculated from $\tau_2 = 7.0$ ps, $\tau_1 = 890$ ps, and $A_{12}/A_{11} = 17.6$ (see Figure 10b).

25DCMIA in MeCN, PrCN, and THF at Different Temperatures. *MeCN.* Picosecond LE and ICT fluorescence decays of 25DCMIA in MeCN were measured from -44 to -20 °C (Table S2, SI). The LE decays have a predominant ultrashort time τ_2 . Even at -44 °C, $\tau_2 = 1.4$ ps (Figure 11a), a time definitely below the experimental time resolution (\approx 3 ps).^{7,10,15,44} That these short decay times can nevertheless be readily observed is caused by the very high amplitude ratio A_{12}/A_{11} (Table S2, SI). As the ICT reaction time generally becomes longer and hence better accessible in solvents less polar than MeCN ($\varepsilon^{25} = 36.7$, $\varepsilon^{-44} = 49.9$), 25DCMIA was investigated in PrCN ($\varepsilon^{25} = 24.2$, $\varepsilon^{-40} = 34.0$) and THF ($\varepsilon^{25} = 7.39$, $\varepsilon^{-60} = 11.0$).⁵⁹ In *n*-hexane ($\varepsilon^{25} = 1.88$), an ICT reaction does not take place (Figure 4c).

PrCN. LE and ICT fluorescence decays in PrCN were measured at temperatures between −40 and −110 °C. The short decay time τ_2 increases from 2.5 ps at −40 °C (Figure 11b) to 5.1 ps at −70 °C (Table S2, SI). In PrCN at lower temperatures (below −75 °C for *N*-phenylpyrrole (PP)),⁵⁷ the solvent dielectric relaxation has to be taken into account, as it starts to interfere with the LE → ICT reaction.

THF. The LE and ICT fluorescence decays at -60 °C are shown in Figure 11c: $\tau_2 = 7.4$ ps, $\tau_1 = 5160$ ps, A = 9.0 (Table S2, SI). The temperature dependence between -60 and -105 °C is presented in Figure 12a. From these data k_a , k_d , and τ'_o (ICT) are calculated (Table S2, SI). Arrhenius plots of these data are depicted in Figure 12b: $E_a = 4.5$ kJ/mol, $E_d = 11.9$ kJ/mol, i.e., $-\Delta H = 7.4$ kJ/mol (Table 14). From the preexponential factors $k_a^0 = 1.6 \times 10^{12} \text{ s}^{-1}$ and $k_d^0 = 1.2 \times 10^{13} \text{ s}^{-1}$, $\Delta S = R \ln(k_a^0/k_d^0) = -17 \text{ J K}^{-1} \text{ mol}^{-1}$ is calculated. Comparable ΔS results have been found for other D/A molecules: $-38 \text{ J K}^{-1} \text{ mol}^{-1}$ (DMABN in MeCN),⁷ $-28 \text{ J K}^{-1} \text{ mol}^{-1}$ (PP in MeCN),⁵⁷ and -23 J K^{-1}

ICT Lifetimes $\tau'_{o}(ICT)$ of 25DCMIA in THF and PrCN. The ICT lifetime $\tau'_{o}(ICT)$ of 25DCMIA in THF decreases when the temperature is lowered: from 4.81 ns at -60 °C to 3.93 ns at -105 °C (Table S2, SI). In PrCN, $\tau'_{o}(ICT)$ similarly decreases from 4.13 ns at -40 °C to 3.78 ns at -101 °C. As $1/\tau'_{o}(ICT) = k'_{f}(ICT) + k'(ISC) + k'(IC)$, this could be caused by $k'_{f}(ICT)$, which becomes larger upon cooling $(k'_{f}(ICT) \propto n^{2})^{58,60-62}_{o}$ whereas k'(ISC) and k'(IC) will decrease or remain unchanged.

Shape of the LE and ICT Picosecond Fluorescence Decay Curves. The LE fluorescence decay curves of the m,n-dicyanoa-nilines in Figures 8-11 have a clearly different shape than the

mnDCMIA	solvent	$\Phi({ m flu})^a$	$ au_1^{\ b} \ [ext{ns}]$	$k_{\rm f}({\rm LE})^c$ or $k'_{\rm f}({\rm ICT})^c [10^7 { m s}^{-1}]$
23DCMIA	<i>n</i> -hexane	0.13	4.08	3.2 (LE)
	DEE	0.25	10.65	2.3 (LE)
	MeCN	0.17	9.77	1.7 (LE)
24DCMIA	<i>n</i> -hexane	0.061	2.27	2.7 (LE)
	DEE	0.051		
	MeCN	0.0025 (LE)		
		0.022 (ICT)	5.46 ^{<i>d,e</i>} (ICT)	0.43^{f} (ICT)
25DCMIA	<i>n</i> -hexane	0.27	9.77	2.8 (LE)
	DEE	0.29	15.8	1.8 (LE)
	THF		7.9	
	EtCN	0.028		
	MeCN	0.0033 (LE)		
		0.025 (ICT)	2.70 (ICT)	0.93 (ICT)
26DCMIA	<i>n</i> -hexane	0.032	1.12^{d}	2.9 (LE)
	DEE		1.90	
	MeCN	0.061	3.74^{d}	1.6 (LE)
34DCMIA	<i>n</i> -hexane	0.16	3.08^{d}	5.2 (LE)
	DEE	0.29	6.75	4.3 (LE)
	MeCN	0.0054 (LE)		
		0.0077 (ICT)	$1.36^{d,g}$ (ICT)	0.57^{h} (ICT)
35DCMIA	<i>n</i> -hexane	0.082	3.50	2.3 LE)
	DEE	0.16		
	MeCN	0.20	15.9	1.3 (LE)

Table 12. Fluorescence Quantum Yields Φ (flu), Nanoseond Decay times τ_1 , and Radiative Rate Constants k_f for the Six mnDCMIAs in *n*-Hexane, DEE, and MeCN at 25 °C

^{*a*} LE fluorescence quantum yield $\Phi(LE)$, unless otherwise indicated. Data for *n*-hexane are from Table 4 and those for MeCN from Table 5. ^{*b*} From nanosecond fluorescence decays, with a time resolution better than 0.5 ns (ref 54). For the picosecond decays of 24DCMIA and 34DCMIA in MeCN, see footnote d. ^{*c*} Radiative rate constant: $k_f = \Phi(flu)/\tau_1$. In the case of the dual fluorescent molecules 24DCMIA, 25DCMIA, and 35DCMIA in MeCN, only approximate values are listed for $k_f(LE)$ and $k'_f(ICT)$, as the expressions for these rate constants are more complex (ref 34). See footnote e. ^{*d*} Time resolution ≈ 3 ps (ref 7). ^{*c*} From Figure 9a. ^{*f*} For 24DCMIA in MeCN, the ICT lifetime $\tau'_o(ICT) = 5.31$ ns (Table 13), hence $k'_f(ICT) = \Phi'(ICT)/\tau'_o(ICT) = 0.41 \times 10^7 \text{ s}^{-1}$. ^{*g*} From Figure 10a. ^{*h*} For 34DCMIA in MeCN, the ICT lifetime $\tau'_o(ICT) = 1.17$ ns (Table 13), and $k'_f(ICT) = \Phi'(ICT)/\tau'_o(ICT) = 0.66 \times 10^7 \text{ s}^{-1}$.

ICT response functions, with a dominant fast decay (τ_2) for LE and a corresponding fast rise for ICT. Some of the decay times τ_2 (Figures 8, 11a, 11b; Tables 13 and S2 (SI)) are shorter than the time resolution⁷ of around 3 ps. Nevertheless, even these decay curves reveal that an ICT reaction takes place, with a reaction time τ_2 below 3 ps. Femtosecond transient absorption experiments with 24DCDMA and 34DCDMA in MeCN, presented in the next section, will allow an accurate view of the temporal evolution of these ICT reactions.

Femtosecond Transient Absorption Spectra in *n*-Hexane and MeCN. Femtosecond transient absorption spectra (at $22 \degree C$) of 24DCDMA in *n*-hexane and MeCN and of 34DCDMA in MeCN were measured to obtain kinetic information on their ICT reactions.

24DCDMA in *n*-Hexane. The transient absorption spectra of 24DCDMA in *n*-hexane are shown in Figure 13a. After correction for bleaching (BL) and stimulated emission (SE), the excited state absorption (ESA) spectra are obtained (Figure 13b), with maxima at 315, 440, 580, and 670 nm (Table 15). A decay is not observed for the band integral BI(300,650) of the ESA spectra between 300 and 650 nm over the range of pump—probe delay times between 0.2 and 100 ps. This means that an LE \rightarrow ICT does not occur. Therefore, the ESA spectrum is attributed to the LE state. The LE spectrum of 24DCDMA is similar to that of DMABN in *n*-hexane, with maxima at 300, 320, 445, and 745 nm (Table 15).⁷ The ESA

maximum of 24DCDMA at 780 nm also appears in the spectrum of TCDMA (Table 15).¹⁵

24DCDMA in MeCN (0.1-9.0 ps). The transient absorption spectra of 24DCDMA in MeCN for pump-probe delay times between 0.1 and 9.0 ps are presented in Figure 14a. After correction for bleaching (BL) and stimulated LE and ICT emission (SE(LE) and SE(ICT)), the excited state absorption (ESA) spectra are obtained (Figure 14b). The ESA spectrum consists of three bands with maxima at 320, 438, and 630 nm (Table 15). Note the appearance of an isosbestic point at around 460 nm: an indication of the presence of two kinetically interacting excited states, LE and ICT. In the ESA spectra, a decay is observed for the absorption maximum at 630 nm, which is hence attributed to LE. A comparable growing-in occurs for the bands with maxima at 320 and 438 nm, which are therefore assigned to the ICT state. A global analysis of the band integrals BI(310,350), BI(410,460), and BI(600,680) in Figure 14c results in a decay time τ_2 of 1.77 ps, with a growing-in (negative A_{2} , eq 10) for BI(410,460), in the spectral range of the ICT absorption.

$$BI = A_2 \exp(-t/\tau_2) + A_0$$
 (10)

24DCDMA in MeCN (0.2–100 ps). The transient absorption spectra of 24DCDMA in MeCN for pump–probe delay times



Figure 8. Picosecond fluorescence decays of 24DCDMA in MeCN at 25 °C, (a) at 400 nm and (b) at 550 nm, with a time resolution of 1.025 ps/ channel and a time window of 1500 effective channels. The 400 nm decay is attributed to LE and that at 550 nm to ICT (see Figure 3b). The LE and ICT decays are analyzed simultaneously (global analysis), resulting in decay times τ_2 and τ_1 with amplitudes A_{1i} (LE) and A_{2i} (ICT) (eqs 7 and 8). The shortest time is listed first. The time $\tau_2 = 1.8$ ps comes from femtosecond transient spectra (Figures 14 and S7 (SI), below) and is kept fixed in the analysis. Excitation wavelength: 298 nm. The time in parentheses is attributed to photoproducts, intrinsic impurities, or experimental problems (see the text). The weighted deviations sigma, the autocorrelation functions A–C, and the values for χ^2 are also indicated.

between 0.2 and 100 ps are shown in Figure S7a in the SI. The ESA spectra, obtained after correction for bleaching (BL) and LE and ICT stimulated emission (SE(LE) and SE(ICT)), are presented in Figure S7b (SI), again with an isosbestic point at around 460 nm. The bands with maxima at 320 and 438 nm show a growing-in, whereas that at 630 nm presents a decay. The first two bands hence belong to the LE ESA spectrum, and the third is part of the ICT ESA spectrum, similar to what was concluded above for 24DCDMA over the time range from 0.1 to 9.0 ps (Figure 14). A global analysis of BI(310,350), BI(410,460), and BI(600,680) in Figure S7c (SI) results in a decay time τ_2 of 1.83 ps, identical to the 1.77 ps from Figure 14c (Table 15).

34DCDMA in MeCN. The transient absorption spectra of 34DCDMA in MeCN for pump—probe delay times between 0.08 and 9.0 ps are shown in Figure 15a. After correction for bleaching (BL) and LE and ICT stimulated emission (SE(LE) and SE(ICT)), the excited state absorption (ESA) spectra are obtained



Figure 9. Picosecond fluorescence decays of 24DCMIA in MeCN at 25 °C, with times τ_i and amplitude $A_{1i}(LE)$ (eq 7): (a) at 390 nm and (b) at 550 nm, both with a time resolution of 0.497 ps/channel and a time window of 1400 effective channels. The 390 nm decay is attributed to LE and that at 550 nm to ICT (see Figure 5b). In (c), the ICT decay with $\tau_1 = 5120$ ps is presented at 10.04 ps/channel. Excitation wavelength: 272 nm. See the caption of Figure 8.

(Figure 15b). The ESA spectra have a main maximum at 330 nm and two smaller maxima at 570 and 635 nm. From a global analysis of BI(315,350), BI(380,430), and BI(610,680) in Figure 15c, a decay time $\tau_2 = 3.1$ ps is determined. The BIs around the maxima at 330 and 635 nm show a decay with a positive amplitude A_2 (eq 10): they belong to the LE state. In the case of BI(380,430) around 385 nm, a growing-in (negative amplitude A_2) is observed. This BI therefore covers the spectral range of the ICT ESA spectrum. Similar ESA spectra are measured with 34DCDMA in MeCN for pump—probe delay times between 0.2 and 100 ps (Figure S8 in SI). From a

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Figure 10. Picosecond LE and ICT fluorescence decays of 34DCMIA in MeCN at (a) 25 °C and (b) -45 °C. The decays were measured at 420 and 580 nm, with a time resolution of 0.497 ps/channel and a time window of 1400 effective channels. The 420 nm decay is attributed to LE and that at 580 nm to ICT (see Figure 5e). The LE and ICT decays are analyzed simultaneously (global analysis), resulting in decay times τ_2 and τ_1 with amplitudes A_{1i} (LE) and A_{2i} (ICT) (eqs 7 and 8). Excitation wavelength: 272 nm. See the caption of Figure 8.

global analysis of three BIs over the same spectral ranges as in Figure 15c, a somewhat longer decay time τ_2 = 4.0 ps is found, likewise with a growing-in for BI(380,430).

Kinetic Analysis of the ESA Decay Times au_2 of 24DCDMA and 34DCDMA in MeCN at 22 °C. From the ESA spectrum of 34DCDMA in MeCN, it is seen that a substantial LE absorption has remained alongside the ICT band at a pump-probe delay of 100 ps (Figure S8c in SI). This is also the case, although to a somewhat smaller extent, for the ESA spectrum of 24DCDMA in MeCN at this long delay time (Figure S7c in SI). The observations show that an LE \rightleftharpoons ICT equilibrium is established. The ICT reaction times τ_2 of 1.8 ps (24DCDMA) and 3.1 ps (34DCDMA) are therefore in fact equal to the reciprocal of the sum of the forward and backward ICT rate constants $1/(k_a + k_d)$, see Scheme 1. A similar equilibrium situation has been encountered with N-(4-cyanophenyl)carbazole (NP4CN).50 For 24DCDMA in MeCN at 25 °C (Table 13), $\tau'_{o}(ICT) = 3.44$ ns, hence $1/\tau'_{o}(ICT) = 0.029 \times 10^{10} \text{ s}^{-1}$. As $k_{d} = 6.5 \times 10^{10} \text{ s}^{-1}$, $k_{d} \gg 10^{10} \text{ s}^{-1}$ τ'_{o} (ICT). Within this so-called high-temperature limit (HTL),⁷ the general expression for $\Phi'(ICT)/\Phi(LE)$ (eq 1) is transformed to eq 2.



Figure 11. Picosecond LE and ICT fluorescence decays of 2SDCMIA in (a) MeCN at -44 °C, (b) PrCN at -40 °C, and (c) THF at -60 °C. The decays were measured at 420 nm (a,b,c), 590 nm (a,b), and 600 nm (c), with a time resolution of 1.978 ps/channel and a time window of 1400 effective channels. The 420 nm decays are attributed to LE and those at 590 and 600 nm to ICT (see Figure 5e). The LE and ICT decays are analyzed simultaneously (global analysis), resulting in times τ_2 and τ_1 with amplitudes A_{1i} (LE) and A_{2i} (ICT) (eqs 7 and 8). Excitation wavelength: 276 nm. See the caption of Figure 8.

Separate Rate Constants k_a and k_d . The separate forward and backward ICT rate constants k_a and k_d (Scheme 1) of 24DCDMA and 34DCDMA in MeCN can be determined by employing the data for the quantum yield ratios $\Phi'(ICT)/\Phi(LE)$,

Table 13.	Fluorescence	Decay Times	and Kinetic	Parameters	(Equations	7 –9, Scheme	for the IC	CT Reaction o	of 24DCDMA,
24DCML	A, 34DCMIA, a	nd 25DCMIA							

mnDCXYA	solvent	$T [^{\circ}C]$	$ au_2 [\mathrm{ps}]$	$ au_1$ [ps]	A_{12}/A_{11} (eq 7)	$k_{\rm a} [10^{10} {\rm s}^{-1}]$	$k_{\rm d} [10^{10} { m s}^{-1}]$	$\tau'_{o}(ICT) [ns]$
24DCDMA	MeCN ^a	25	1.8^b	3800 ^c	7.6	49.1	6.5	3.44
34DCDMA	DEE	-101^{d}	18	9250	19.9	5.28	0.26	9.08
24DCMIA	MeCN ^e	25	3.0	5460	24.4	32.0	1.3	5.31
	DEE	25	3.4	5250	5.9	25.2	4.3	4.73
	DEE	-45	4.8	5860	24.9	20.0	0.80	5.72
	DEE	-115	21.8	5470	75.2	4.5	0.060	5.42
34DCMIA	MeCN ^f	25	4.6	1360	5.5	18.4	3.3	1.17
	MeCN ^g	-45	7.0	890	17.6	13.5	0.76	0.85
25DCMIA	$MeCN^{h}$	-44	1.4	2340	114	70.8	0.62	2.32

^{*a*} Figure 8. ^{*b*} From femtosecond ESA spectra (Figures 14 and S7 (SI)). ^{*c*} See Table 11. ^{*d*} ICT reaction possible because of the increase in solvent polarity upon cooling: $\varepsilon^{-110} = 9.79$, $\varepsilon^{25} = 4.24$. ^{*e*} Figure 9a. ^{*f*} Figure 10a. ^{*g*} Figure 10b. ^{*h*} Figure 11a.



Figure 12. 25DCMIA in THF. (a) Fluorescence decay times (τ_2 , τ_1) and the LE amplitude ratio $A = A_{12}/A_{11}$ (eqs 7–9) as a function of temperature and (b) Arrhenius plots of the ICT rate constants (k_a , k_d) and τ'_0 (ICT), see Scheme 1. $\Delta H = (E_a - E_d) = -7.4$ kJ/mol, $k_a^0 = 1.6 \times 10^{12} \text{ s}^{-1}$, $k_d^0 = 1.2 \times 10^{13} \text{ s}^{-1}$, and $\Delta S = R \ln(k_a^0/k_d^0) = -17 \text{ J K}^{-1}$ mol⁻¹ (Table 14).

Table 14. Thermodynamic Parameters of the ICT Reactionof 25DCMIA in THF

$E_{\rm a}$	$E_{\rm d}$	$-\Delta H$	$k_{\rm a}^{0}$	$k_{\rm d}^{0}$	$-\Delta S$
[kJ/mol]	[kJ/mol]	[kJ/mol]	$[10^{12} \mathrm{s}^{-1}]$	$[10^{12} \text{ s}^{-1}]$	$[JK^{-1} mol^{-1}]$
4.5	11.9	7.4	1.55	11.7	16.8

under HTL conditions (eq 2). In this procedure, $k'_{\rm f}(\rm ICT)/k_{\rm f}(\rm LE)$ is needed. For DMABN in MeCN at 25 °C, $k'_{\rm f}(\rm ICT)/k_{\rm f}(\rm LE) = 0.12,^7$ whereas for DIABN in *n*-hexane at 25 °C, ${}^{51}k'_{\rm f}(\rm ICT)/k_{\rm f}(\rm LE) = 0.17$. Also for PP in MeCN at 25 °C, $k'_{\rm f}(\rm ICT)/k_{\rm f}(\rm LE)$ is much smaller (0.19) than unity.³⁴

The mean value of $k'_{\rm f}(\rm ICT)/k_{\rm f}(\rm LE) = 0.15$ from the data for DMABN and DIABN is adopted here for 24DCDMA and 34DCDMA. For 24DCDMA, with $\Phi'(\rm ICT)/\Phi(\rm LE) =$ $k'_{\rm f}(\rm ICT)/k_{\rm f}(\rm LE)$, $k_{\rm a}/k_{\rm d} = 1.2$ (Table 3), then $k_{\rm a}/k_{\rm d} = 8.0$. Together with $(k_{\rm a} + k_{\rm d}) = 1/\tau_2 = 1/(1.8 \text{ ps}) = 56 \times 10^{10} \text{ s}^{-1}$ (Figures 14c and S7c (SI)), one obtains: $k_{\rm a} = 49 \times 10^{10} \text{ s}^{-1}$ and $k_{\rm d} = 6.2 \times 10^{10} \text{ s}^{-1}$ (Table 15). These data are practically



Figure 13. 24DCDMA in *n*-hexane at 361 nm excitation (spectral range: 295–683). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra, at pump-probe delay times between 0.2 and 100 ps, after correction for bleaching (BL) and stimulated emission (SE). The BL and SE (LE, cf Figure 2b) spectra are also depicted. (c) For the band integral BI(300,650), between 300 and 650 nm in the ESA spectrum, a decay is not found between 0.2 and 100 ps: an ICT reaction does not take place. $m\Delta$ OD is the optical density/1000.

the same as those (49 and $6.5 \times 10^{10} \text{ s}^{-1}$) derived from the LE and ICT fluorescence decay parameters τ_2 , τ_1 , and A_{12}/A_{11} (Table 13). Similarly, for 34DCDMA with

Table 15. Excited	State Absorption ((ESA) Maxima	(in nm) and H	ESA Decay Times (in ps) o	f 24DCDMA and	l 34DCDMA at 22 °	C"
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	solvent	ESA maxima (nm)	$ au_2 [\mathrm{ps}]$	$(k_{\rm a} + k_{\rm d})^b [10^{10} {\rm s}^{-1}]$	$k_{\rm a} [10^{10} {\rm s}^{-1}]$	$k_{\rm d} [10^{10} {\rm s}^{-1}]$
24DCDMA	<i>n</i> -hexane ^c	315, 440, 670	-	-	-	-
	$MeCN^d$	320, 438, 630	1.8	55.6	49.4	6.2
34DCDMA	MeCN ^e	330, 385, 635	3.1	32.3	22.5	9.8
$DMABN^f$	<i>n</i> -hexane	300, 320, 445, 745 (LE)				
	MeCN	320, 355, 440, 710 (LE) 315, 425 (ICT)	4.07	24.1	24.0	0.047
TCDMA ^g	MeCN	310, 335, 510, 580 (LE)				
$PCDMA^{h}$	MeCN	290, 380, 520 (LE)				

^{*a*} See Figures 13–15 and S7 and S8 (SI). Data for TCDMA and DMABN, TCDMA, and PCDMA are included for comparison. ^{*b*} ($k_a + k_d$) = 1/ τ_2 (see text). ^{*c*} Figure 13. ^{*d*} Figures 14 and S7 (SI). ^{*c*} Figures 15 and S8 (SI). ^{*f*} Ref 7. ^{*g*} Ref 15. ^{*h*} Ref 10.



Figure 14. 24DCDMA in MeCN at 361 nm excitation (305–683 nm). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra, at pump-probe delay times between 0.1 and 9.0 ps. A decay is observed for the absorption maximum at 630 nm, attributed to LE. A growing-in occurs for the maxima at 320 and 438 nm, which are assigned to the ICT state. (c) A global analysis of the band integrals BI(310,350), BI(410,460), and BI(600,680) results in a decay time τ_2 of 1.77 ps, with a growing-in (negative A_2 , eq 10) for BI(410,460), in the spectral range of the ICT absorption. See the caption of Figure 13.

 $\Phi'(\text{ICT})/\Phi(\text{LE}) = 0.35$ (Table 3), k_a/k_d becomes equal to 2.3. From $k_a + k_d = 1/\tau_2 = 1/(3.1 \text{ ps}) = 32 \times 10^{10} \text{ s}^{-1}$ (Figure 15c and S8c (SI)), one so finds $k_a = 23 \times 10^{10} \text{ s}^{-1}$ and $k_d = 9.5 \times 10^{10} \text{ s}^{-1}$ (Table 15).

The lower k_a and larger k_d values of 34DCDMA as compared with 24DCDMA point to a smaller ICT reaction enthalpy difference $-\Delta H$ for 34DCDMA, which causes the LE \rightleftharpoons ICT equilibrium to be shifted further toward LE. This also follows



Figure 15. 34DCDMA in MeCN at 361 nm excitation (305–683 nm). (a) Transient absorption spectra and (b) excited state absorption (ESA) spectra, at pump-probe delay times between 0.08 and 9.0 ps. A decay is observed for the absorption maxima at 330 and 630 nm, attributed to LE. A growing-in occurs around 385 nm, which is assigned to the ICT state. (c) A global analysis of the band integrals BI(315,350), BI(380,430), and BI(610,680) results in a decay time τ_2 of 3.1 ps, with a growing-in (negative A_2 , eq 10) for BI(380,430), in the spectral range of the ICT absorption. See the caption of Figure 13.

from $\Phi'(ICT)/\Phi(LE)$: 0.35 for 34DCDMA and 1.2 for 24DCDMA (Table 3).

CONCLUSIONS

The fluorescence spectra of the six isomers of mnDCDMA and mnDCMIA in *n*-hexane consist of a single LE fluorescence band. This means that an LE \rightarrow ICT reaction does not take place

in this solvent, although the dicyanobenzene subgroups in the dicyanoanilines are considerably better electron acceptors than the benzonitrile moiety in DMABN, for which ICT just starts to occur in *n*-hexane. The larger electron affinity can be deduced from the reduction potentials $E(A^{-}/A)$ vs SCE: -1.68 V (1,2-dicyanobenzene), -1.95 V (1,3-dicyanobenzene), and -1.63 V (1,4-dicyanobenzene) as compared with -2.36 V for benzonitrile. In MeCN, four of the mnDCDMAs (mn = 23, 25, 26, 35) and three of the mnDCMIAs (mn = 23, 26, 35) likewise only show an LE emission, whereas dual LE + ICT emission is observed with 24DCDMA and 34DCDMA, as well as with 24DCMIA and 34DCMIA and to a smaller extent also with 25DCMIA. The occurrence of an LE \rightarrow ICT reaction with the 2,4- and 3,4-dicyanoanilines is connected with the magnitude of the energy gap $\Delta E(S_1, S_2)$, which is much smaller for these molecules than for the other isomers: 4870 and 4690 cm^{-1} for 24DCDMA and 24DCMIA against 8650 cm^{-1} for 23DCMIA in MeCN, as an example. By comparison, for DMABN, the prototype of a D/A molecule undergoes an ICT reaction, $\Delta E(S_1, S_2) =$ 2700 cm⁻¹, in *n*-hexane. The observation that ICT is more efficient (larger $\Phi'(ICT)/\Phi(LE)$) for 24DCMIA and 34DCMIA than with 24DCDMA and 34DCDMA is due to the stronger electron donor character (smaller $(E(D/D^+) \text{ vs SCE})$ of $iPrN(Me)_2$ (0.84 V) than that of N(Me)₃ (1.05 V). With 25DCMIA in MeCN, ICT fluorescence is observed, notwithstanding its relatively large $\Delta E(S_1, S_2)$ of 9240 cm⁻¹. This is caused by the fact that 25DCMIA has a strongly twisted amino group $(\theta = 42.6^{\circ})$, which leads to electronic decoupling of the D and A subunits, making the molecule react as an intermolecular exciplex. Under such conditions, $\Delta E(S_1,S_2)$ is no longer a criterion for the appearance of an LE \rightarrow ICT reaction. For the other dicyanoanilines showing dual (LE + ICT) fluorescence, the angle θ is much smaller, 13.9° (24DCDMA), 16.7° (24DCMIA), and 2.9° (34DCMIA), and $\Delta E(S_1,S_2)$ remains an essential factor for the appearance of dual fluorescence in these strongly coupled D/A systems.

The dipole moments $\mu_e(ICT)$ are 13 D for 24DCDMA and 16 D for 34DCDMA, whereas for 24DCMIA and 34DCMIA slightly larger values are determined: 15 and 18 D. The corresponding $\mu_e(LE)$'s are somewhat smaller, with 11 and 15 D for 24and 34DCDMA and 12 and 16 D for 24- and 34DCMIA. With 25DCMIA, smaller dipole moments are measured: $\mu_e(ICT) = 11$ D and $\mu_e(LE) = 9$ D. The differences between $\mu_e(ICT)$ and $\mu_e(LE)$ of the dicyanoanilines are smaller than for DMABN, with $\mu_e(ICT) =$ 17 D and $\mu_e(LE) = 10$ D. This is probably caused by the different dipole moment directions in the ICT and LE states of the former molecules. The change in enthalpy difference $\Delta H(SB)$ of the ICT reaction in MeCN, obtained from plots of $\ln(\Phi'(ICT)/\Phi(LE))$ vs 1000/*T*, is relatively small: -5.4 kJ/mol (24DCDMA), -4.7 kJ/mol (24DCMIA), and -3.9 kJ/mol (34DCMIA).

Picosecond LE and ICT fluorescence decays are determined for 24DCDMA, 24DCMIA, 34DCMIA, and 25DCMIA in a number of solvents at various temperatures. From these decays, the forward and backward ICT rate constants k_a and k_d and also the ICT lifetime $\tau'_o(ICT)$ are calculated. From the temperature dependence of k_a and k_d for 25DCMIA in THF, the activation energies $E_a = 4.5$ kJ/mol and $E_d = 11.9$ kJ/mol are obtained, giving $\Delta H = -7.4$ kJ/mol.

The femtosecond ESA spectra of 24DCDMA and 34DCDMA in MeCN at 22 °C consist of a superposition of LE and ICT absorptions, showing that an LE \rightleftharpoons ICT equilibrium is established in around 4 ps. The ICT reaction time, derived from the decay time τ_2 of the LE and the rise of the ICT absorption bands, is 1.8 ps for 24DCDMA and 3.1 ps for 34DCDMA. The reciprocal of this time τ_2 is equal to $(k_a + k_d)$. By combining these results with the data for the fluorescence decays and $\Phi'(ICT)/\Phi(LE)$, the values $k_a = 49 \times 10^{10} \text{ s}^{-1}$ (24DCDMA) and $k_a = 22.6 \times 10^{10} \text{ s}^{-1}$ (34DCDMA) are determined.

ASSOCIATED CONTENT

Supporting Information. Crystal structure; fluorescence and absorption spectra; oxidation potentials; solvatochromic plots; ESA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(1) Definition of LE and ICT. The term LE (locally excited) may lead to confusion in the discussion of ICT reactions. It originated from *inter*molecular exciplex formation, where the excitation in the ${}^{1}A^{*} + D \rightarrow$ ${}^{1}(A^{-}D^{+})$ reaction is initially localized on the monomer ${}^{1}A^{*}$ and becomes more delocalized over the molecules A and D upon exciplex formation. When a donor (D)/acceptor (A) compound only emits a single fluorescence band, we call this an emission from an LE state, irrespective of the dipole moment $\mu_{e}(LE)$ of this state. An example is DMABN in *n*-hexane, with $\mu_{\rm e}({\rm LE}) = 10 \text{ D}$ as compared with $\mu_{\rm g}({\rm S}_0) = 6.6 \text{ D}$ (refs 7 and 21). In such a case, we say that an ICT reaction did not take place upon excitation, although a substantial increase in charge separation in fact occurs: $\Delta \mu \approx 3.4$ D. We do speak of an ICT reaction only when a new excited ICT state is produced from the relaxed initially excited $S_1(LE)$ state as the precursor. For this ICT state, the condition $\mu_{e}(ICT) > \mu_{e}(LE)$ generally holds, such as for DMABN in polar solvents with dipole moments of \approx 17 D (ICT) and \approx 9 D (LE) (ref 52). In the present article, the increase in dipole moment during the $LE \rightarrow ICT$ reaction is rather small, around 2 D for 24DCDMA and 34DCDMA (Table 8) and 3 D for 24DCMIA, 25DCMIA, and 34DCMIA (Table 10). For these molecules, an ICT reaction nevertheless occurs: two excited states, LE and ICT, are observed.

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