

ON THE ELECTRONIC STRUCTURE OF EXCIPLEXES IN α -(1- OR 2-NAPHTHYL)- ω -*N,N*-DIALKYLAMINOALKANES[†]

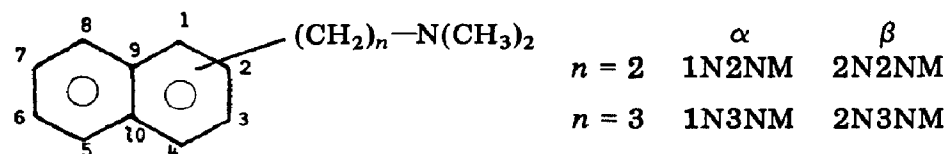
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Summary

In this paper the theoretical model for the electronic structure of an exciplex with aromatic donors and acceptors, developed by Weller and modified for intramolecular exciplexes in which a parasubstituted phenyl acts as acceptor and an aliphatic amine as donor, is applied to compounds of type I:



This model allows the exciplex geometry to be estimated and values for the emission maximum and the fluorescence rate constant which approach the experimental observed values of these quantities within the experimental error to be determined. The influence of the solvent polarity can also be mimicked. These data show a substantial difference between 1-dimethylamino-2-(1-naphthyl)ethane (1N2NM) and 1-(dimethylamine)-2-(2-naphthyl)ethane (2N2NM) as to the nature of the excited state exciplex in solvents of low polarity.

1. Introduction

The electronic structure of exciplexes [1] or charge transfer (CT) complexes [2 - 4] between aromatic donors and acceptors and the electronic structure of excimers [5] has been investigated by several workers. Changing the relative energy of the locally excited states and the CT state allows a gradual change from a completely non-polar excimer to an exciplex

[†] Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

characterized by the CT state. These exciplexes obtain their transition dipole moments from mixing the CT states with either the locally excited state [1 - 4] or the ground state [6]. Although the latter interaction makes a relatively unimportant contribution to the exciplex energy, in several cases it makes an important contribution to the exciplex oscillator strength. The theoretical model developed by Beens and Weller [1] and Iwata *et al.* [4] for complexes with aromatic donors has been extended to complexes with aliphatic donors [7, 8]. Linking both chromophores by an ethane or a propane chain severely limits the relative positions and orientations of donors and acceptors [9] and reduces the number of geometric structures that must be considered. The emission of intramolecular exciplexes with an aliphatic donor has been observed for naphthalene [10, 11], phenyl [12, 13] or a substituted phenyl [14, 15] or pyrene [16] as an acceptor. Calculations have been applied to intramolecular exciplexes with parasubstituted phenyls as acceptors [7]. In this paper this approach is extended to exciplexes with naphthalene (1 or 2) as the acceptor. It is possible in this theoretical framework to rationalize the influence of the chain length, the substitution site on the nucleus and the solvent polarity on the exciplex emission properties.

2. The model

Since a detailed discussion of the model has been reported elsewhere [7], only the general line of thought is presented.

2.1. The zeroth-order orbitals

Hückel molecular orbitals (MOs) are used as the zeroth-order orbitals for the aromatic moiety, which acts as an acceptor. The Hückel MOs are built from single Slater-type orbitals (STOs) with an effective charge of 3.25. By making the appropriate linear combination of products of these orbitals the ground state and the first four excited states of naphthalene are obtained [17, 18].

The $2p_z$ (STO with an effective charge of 3.9) and 3s (sum of four STOs) [19] orbitals of nitrogen are used as the ground state and first excited state respectively of the amine. By constructing Slater determinants corresponding to the different configurations and taking the appropriate linear combination of these determinants it is possible to obtain the zeroth-order approximations for the ground state (only one determinant), the locally excited singlet states and the singlet CT levels. The zeroth energies are calculated from the diagonal elements of the F operator [20].

In the zeroth-order approximation only interaction between the singlet excited states or between the two lowest CT states will be important.

2.2. Interactions in the presence of overlap

Overlap between the orbitals of the naphthyl and the nitrogen will induce interactions between the CT state and the various zeroth-order

locally excited states. The non-diagonal matrix elements of the F operator are calculated using the Mulliken approximation [21]. To evaluate the Coulomb integrals the complete neglect of differential overlap (CNDO) approximation is used [22] in the non-diagonal matrix elements. Correction for the non-orthogonality of the zeroth-order orbitals [21] of the donor (D) and acceptor (A) is applied. The overlap integrals which give a qualitative picture of the interactions are presented in Table 1 for the most important configurations of the compounds with two and three CH_2 groups in the alkyl chain (for an explanation of the notation of the configurations, see Section 2.1).

TABLE 1
Overlap integrals

	$S(2p_N, \psi_4)$	$S(2p_N, \psi_5)$	$S(2p_N, \psi_6)$	$S(3s_N, \psi_6)$
1N2NM	-0.0083	0.0191	-0.0182	0.0056
2N2NM	0.0302	0.0231	0.0121	-0.0014
1N3NM (i)	-0.0272	0.0197	-0.0184	0.0057
1N3NM (ii)	-0.0261	0.0057	-0.0054	0.0017
1N3NM (iii)	0.0281	0.0426	-0.0078	0.0037
1N3NM (iv)	0.0404	0.0443	0.0054	0.0006
2N3NM (i)	0.0300	0.0393	-0.0040	0.0024
2N3NM (ii)	0.0484	0.0322	0.0143	-0.0022

ψ_4 and ψ_5 are the two highest occupied orbitals of naphthalene and ψ_6 is the lowest unoccupied orbital of naphthalene.

1N2NM is 1-(dimethylamino)-2-(1-naphthyl)ethane; 2N2NM is 1-(dimethylamino)-2-(2-naphthyl)ethane; 1N3NM is 1-(dimethylamino)-3-(1-naphthyl)propane; 2N3NM is 1-(dimethylamino)-3-(2-naphthyl)propane.

See Section 3.1 for definitions of (i), (ii), (iii) and (iv).

2.3. The parametrization

To calculate the various energy levels and wavefunctions it is necessary to know the atomic coordinates [7] and electronic parameters such as the various singlet energies, the donor ionization potentials IP_D [7] and the electronic affinity of the acceptor EA_A .

2.3.1. Atomic coordinates

The position of the nitrogen relative to the naphthyl is restricted by the alkyl chain linking both chromophores and is completely determined by the various dihedral angles in the chain.

2.3.2. The excitation energies

The excitation energies of the naphthyl derivatives are obtained from ref. 23 (Table 2). The excitation energy of the amine is determined from the emission maximum in isopentane. This emission maximum gives the energy difference between the S_0 and S_1 hypersurfaces in planar geometry. The calculation of the transition dipoles from the extinction coefficients or fluorescence rate constants is presented in Section 2.4.2.

TABLE 2

Values of the excitation energies of α - and β -methylnaphthalene

	$E(L_a)$ (eV)	$E(L_b)$ (eV)	$E(B_b)$ (eV)
α -methylnaphthalene	4.40	3.98	5.53
β -methylnaphthalene	4.51	3.88	5.53

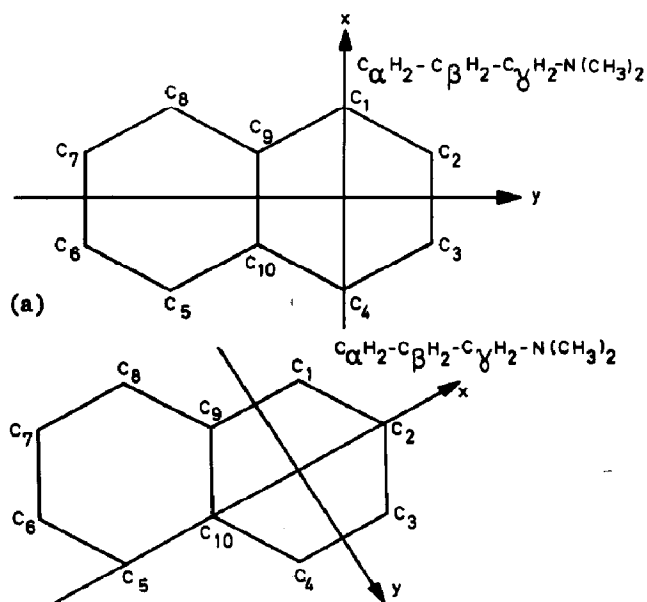


Fig. 1. Atomic parameters of the exciplex with substitution in (a) the 1 position and (b) the 2 position.

2.4. Correlation with experimental parameters

2.4.1. Emission energy

The difference between the exciplex energy and the energy of the ground state depends on the geometrical arrangement of the exciplex and therefore corresponds to the maximum of the exciplex emission. It is equal to the difference between the lowest and the second-lowest eigenvalue of the following matrix [7]:

$$\begin{bmatrix} E(AD) = 0 & \langle A^-D^+ | H | AD \rangle & 0 & 0 & 0 \\ \langle AD | H | A^-D^+ \rangle & E(A^-D^*) & \langle AD^* | H | A^-D^+ \rangle & \langle A_p D | H | A^-D^+ \rangle & \langle A_\alpha D | H | A^-D^+ \rangle \\ 0 & \langle A^-D^+ | H | AD^* \rangle & E(AD^*) & 0 & 0 \\ 0 & \langle A^-D^+ | H | A_p D \rangle & 0 & E(A_p D) & 0 \\ 0 & \langle A^-D^+ | H | A_\alpha D \rangle & 0 & 0 & E(A_\alpha D) \end{bmatrix}$$

$$E(A^-D^*) = IP_D - EA_A - C \quad (1)$$

where $IP_D = 7.7$ eV, $EA_A = -0.20 \pm 0.2$ eV [24] and $C = \langle \varphi_6 \varphi_6 | 2p_N 2p_N \rangle$ is the Coulomb integral between the lowest unoccupied molecular orbital (LUMO) of naphthalene φ_6 and the 2p orbital of nitrogen $2p_N$.

The value of IP_D [7] is commented on in the previous section.

2.4.2. Fluorescence rate constant

The pre-exponential factor A_5 of the fluorescence rate constant is given by [7]

$$A_5 = 2.1 \times 10^{-5} (\tilde{\nu}_{\max})^3 \{ b_1 \langle \varphi(AD) | r | \varphi(AD) \rangle + b_2 \langle \varphi(AD) | r | \varphi(A^-D^+) \rangle + b_3 \langle \varphi(AD) | r | \varphi(AD^*) \rangle + b_4 \langle \varphi(AD) | r | \varphi(A_p D) \rangle + b_5 \langle \varphi(AD) | r | \varphi(A_\alpha D) \rangle + a_2 b_2 \langle \varphi(A^-D^+) | r | \varphi(A^-D^+) \rangle \}^2 \quad (2)$$

In this equation $\tilde{\nu}$ is expressed in reciprocal centimetres and the transition dipole moments in ångströms. $(\tilde{\nu}_{\max})^3$ is an approximation of the average of $\tilde{\nu}^3$ over the emission band. The coefficients a_i and b_j represent the eigenvectors belonging to the lowest and the second-lowest eigenvalues respectively of the matrix $\langle \varphi_i | H | \varphi_j \rangle$. $\langle \varphi(AD) | r | \varphi(AD) \rangle$ is the dipole moment of the exciplex ground state; this term and the second term are very small and can be neglected. $\langle \varphi(A^-D^+) | r | \varphi(A^-D^+) \rangle$ represents the exciplex dipole moment ($r \approx 3 \pm 0.2$ Å). $\langle \varphi(AD) | r | \varphi(AD^*) \rangle$ is the transition dipole moment of the $S_1 \rightarrow S_0$ transition of the amine and has a value of 0.2 Å. $\langle \varphi(AD) | r | \varphi(A_p D) \rangle$ and $\langle \varphi(AD) | r | \varphi(A_\alpha D) \rangle$ are the transition dipole moments of the L_a and L_b transitions respectively of the naphthyl chromophores (Table 3). They are calculated using the oscillation strength of the transition and the fluorescence rate constant.

TABLE 3

Transition dipole moments of the naphthalene chromophores

	$f(L_a)$	$\tilde{\nu}(L_a)$ (cm^{-1})	$M(L_a)$ (Å)	$k_F(L_b)$ (s^{-1})	$\tilde{\nu}(L_b)$ (cm^{-1})	$M(L_b)$ (Å)
α -methylnaphthalene	0.18	35500	0.68	3.1×10^6	32100	0.067
β -methylnaphthalene	0.18	36400	0.67	4.5×10^6	31300	0.084

The data were taken from refs. 23 and 25.

3. Results and discussion

3.1. Estimation of the exciplex geometry

The exciplex geometry is estimated by calculating the emission maximum of the exciplex for various conformations of the alkyl chain. The p_z orbital of the nitrogen is assumed to be in the xz plane and the naphthyl is assumed to be in the xy plane. Large deviations from this geometry will

lead to repulsive interactions between the naphthyl hydrogens and the CH_3 groups attached to the nitrogen and the CH_2 groups of the alkyl chain.

The observed emission energy for the 1N2NM system corresponds to an eclipsed -25° geometry (Fig. 2(a) and Fig. 3, curve a). For this geometry

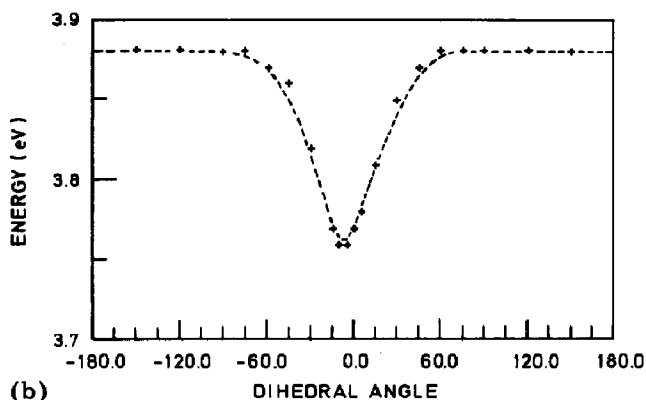
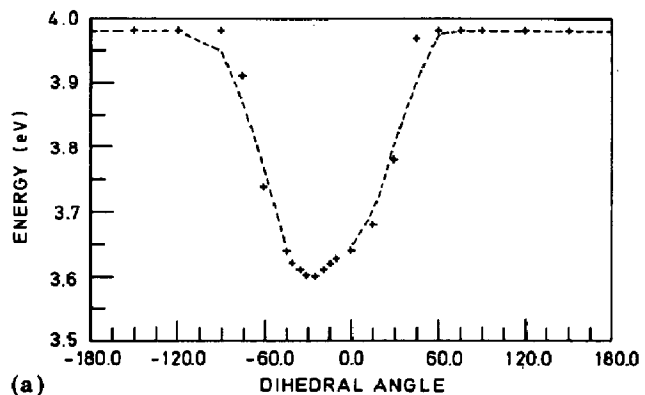


Fig. 2. The influence of the dihedral angle on the emission maxima of (a) 1N2NM and (b) 2N2NM in low polarity medium.

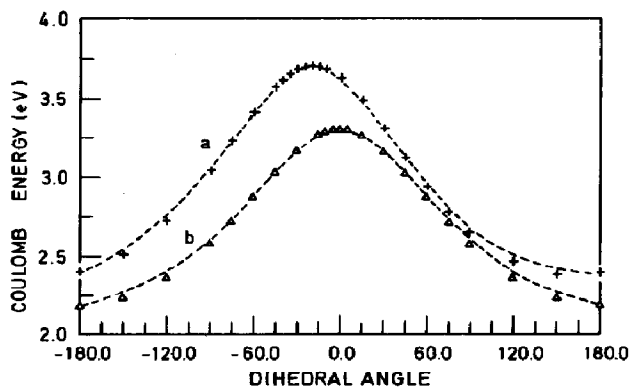


Fig. 3. The influence of the dihedral angle on the Coulomb attraction between the naphthalene LUMO φ_6 and N^+ for 1N2NM (curve a) and 2N2NM (curve b).

the exciplex dipole has a value of 16 debyes. The best geometry for the 2N2NM system is obtained for a dihedral angle of -10° (Fig. 2(b) and Fig. 3, curve b). Since the nitrogen cannot approach the ring as closely in this compound, it will rotate a little to optimize the overlap. The exciplex dipole has a value of 20 debyes and is larger than that for the corresponding 1-naphthyl compound because the charges are farther away from each other. Computer drawings of the optimum geometry for 1N2NM and 2N2NM are shown in Figs. 4 and 5 respectively. Examination of Figs. 2(a) and 2(b) reveals that the depth of the potential well is 0.4 eV for 1N2NM compared with 0.15 eV for 2N2NM, while the width for 2N2NM is much less than that for 1N2NM. From this it can be concluded that 1N2NM is much more stabilized when the conformation approaches the geometry of the exciplex and that a much narrower stabilizing geometry is available for 2N2NM.

The most favourable conformation for 1N2NM is still 0.25 eV lower than that for 2N2NM. This can be explained by the fact that the overlap possibilities of the 1-naphthyl compound are better than those of the 2-naphthyl compound.

In the propane systems several conformations are compatible with the observed emission energy. However, some of these can be excluded because the distance between the nitrogen and the plane of the naphthyl group (z direction) is less than 2.25 Å which will result in a strong repulsive interaction between the two chromophores.

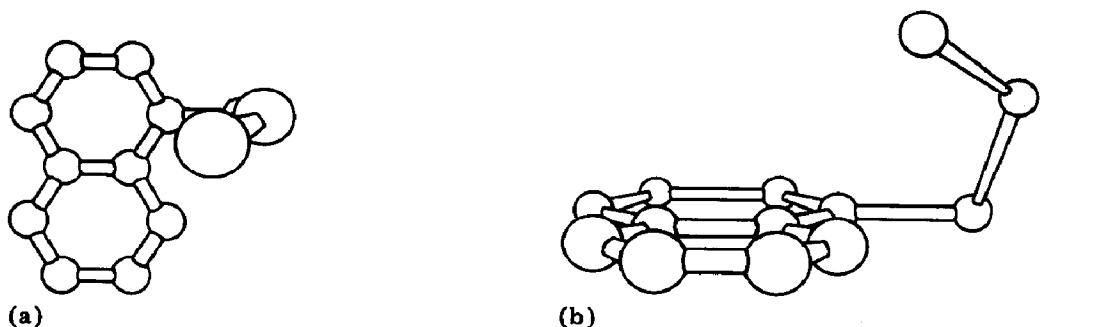


Fig. 4. Geometry of (a) the 1N2NM exciplex (in the xy plane) and (b) the 1N2NM exciplex (in the xz plane).

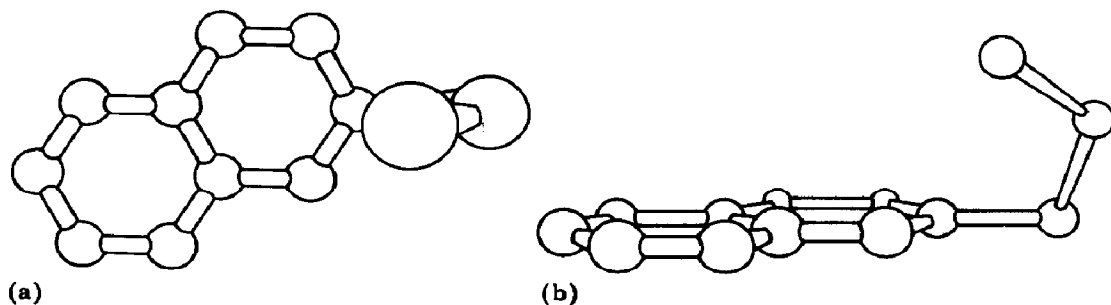


Fig. 5. Geometry of the 2N2NM exciplex in (a) the xy plane and (b) the xz plane.

Four conformations are possible for 1N3NM: (i) $\theta_{\alpha\beta} = 15^\circ$, $\theta_{\beta\gamma} = -70^\circ$; (ii) $\theta_{\alpha\beta} = -60^\circ$, $\theta_{\beta\gamma} = 75^\circ$; (iii) $\theta_{\alpha\beta} = -15^\circ$, $\theta_{\beta\gamma} = 70^\circ$; (iv) $\theta_{\alpha\beta} = 60^\circ$, $\theta_{\beta\gamma} = -65^\circ$. $\theta_{\alpha\beta}$ is the angle between the planes $C_1C_\alpha C_\beta$ and $C_\alpha C_\beta C_\gamma$ and $\theta_{\beta\gamma}$ is the angle between the planes $C_\alpha C_\beta C_\gamma$ and $C_\beta C_\gamma N$. Conformation (i) gives the best overlap and is taken below as an example (Fig. 6). The exciplex dipole moment is 13 debyes which is less than that of 1N2NM. This is because the additional CH_2 group enables the nitrogen to fold better and further over the ring.

Two conformations remain to be considered for 2N3NM: (i) $\theta_{\alpha\beta} = -45^\circ$, $\theta_{\beta\gamma} = 70^\circ$; (ii) $\theta_{\alpha\beta} = 30^\circ$, $\theta_{\beta\gamma} = -65^\circ$. The first of these is taken below as an example (Fig. 7). The dipole moment is 16 debyes which is larger than that of 1N2NM but smaller than that of 2N2NM.

The relative values of the calculated dipole moments correspond to the relative experimental values of μ^2/ρ^3 [26]. The calculation shows further that the coulombic attraction term is extremely important in the stabilization of the complex [26] (Fig. 3).

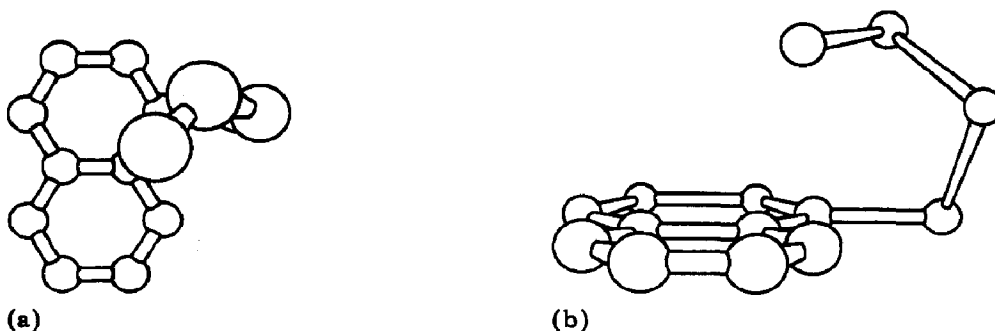


Fig. 6. Geometry of the 1N3NM (i) exciplex in (a) the xy plane and (b) the xz plane.

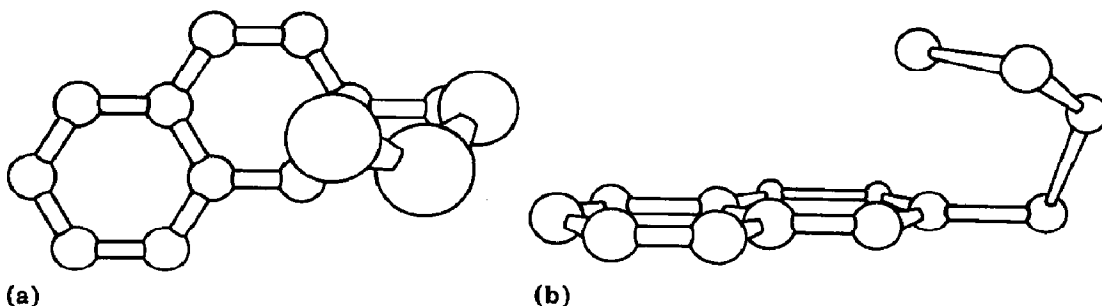


Fig. 7. Geometry of the 2N3NM (i) exciplex in (a) the xy plane and (b) the xz plane.

3.2. Energetics

The calculated energies of the exciplexes studied are summarized and compared with the experimental values in Table 4.

It can be seen that the exciplexes formed by 1N2NM have lower energies $h\nu_{\text{max calc}}$ than those formed by 2N2NM, but that this difference between 1 and 2 substitution is diminished within the propane systems.

TABLE 4
Energetics of the naphthylalkylamine exciplexes

	$h\tilde{\nu}_{\text{max obs}}$ (eV)	$h\tilde{\nu}_{\text{max calc}}$ (eV)	$\Delta E(0)^b$ (eV)	$E_{\text{ex}} - E_{\text{CT}}^c$ (eV)	E_{CT} (eV)
1N2NM	3.44	3.60	-0.039	-0.04	3.54
2N2NM	3.59	3.76	-0.015	-0.13	3.83
1N3NM	3.16	3.18	-0.045	-0.04	3.14
2N3NM	3.16	3.23	-0.002	-0.15	3.35

^aThe experimental data are for piperidine as donor (more donor capacity and therefore a lower expected energy). The solvent was isoctane at room temperature.

^bStabilization of the exciplex ground states *versus* the zeroth-order ground level.

^cStabilization of the exciplex *versus* the zeroth-order CT level E_{CT} .

The deviation between the observed and the calculated values of the emission frequency is at most 5%.

For the 1-naphthyl compounds in the exciplex, stabilization relative to the CT level by interaction with the locally excited state is almost completely compensated by its destabilization by interaction with the ground state. Therefore the net stabilization or destabilization of the exciplex *versus* the zeroth-order CT level in these systems is always less than 0.1 eV ($E_{\text{ex}} - E_{\text{CT}}$ in Table 4).

For the 2-naphthyl compounds there is a strong interaction with locally excited states, so that $E_{\text{ex}} - E_{\text{CT}}$ is generally greater for these systems.

The stabilization of the ground state was quite small in all systems studied.

3.3. The electronic structure of the exciplex

The contributions of the various zeroth-order states to the exciplex are given in Table 5. They are calculated as the square of the corresponding coefficients in the exciplex wavefunction. Table 5 also gives the contribution of the CT level to the (repulsive) exciplex ground state. The exciplex is always more than 90% CT for the 1-substituted naphthyl compounds.

There is a marked difference between the 1-naphthyl- and 2-naphthyl-substituted ethane systems. The 2N2NM exciplex has only 29% CT; the

TABLE 5
Contributions of the various zeroth-order levels to the exciplex

	CT(gr) (%)	CT(ex) (%)	AD(ex) (%)	AD*(ex) (%)	$A_{\beta}D(\text{ex})$ (%)	$A_{\alpha}D(\text{ex})$ (%)
1N2NM	1.0	92.2	1.0	0.5	4.8	1.7
2N2NM	0.4	29.2	0.2	0.02	2.6	67.2
1N3NM	1.4	92.2	1.4	0.2	2.3	4.4
2N3NM	0.06	84.6	0.05	0.04	7.8	8.4

majority consists of $A_\alpha D$. This is due to the poorer overlap in the 2N2NM system. This difference is reduced in the propane systems although the percentage CT character is still lower for the 2-substituted compounds. Mixing with the lowest excited acceptor state, *i.e.* $A_\alpha D$, occurs. There is no mixing with the excited donor because AD^* lies too high in energy. This is an obvious difference from the phenyldimethylaminoalkanes [5].

3.4. The fluorescence rate constant

In Table 6 A_5 represents the pre-exponential factor of the exciplex fluorescence rate constant, $A_5(AD)$ is the value of A_5 if only mixing of A^-D^+ in the ground state contributes, $A_5(AD^*)$ is the value of A_5 if only mixing with D^* contributes, $A_5(A^-D^+)$ is the value of A_5 if only $\langle\varphi(A^-D^+)|r|\varphi(AD)\rangle$ contributes, $A_5(-A^*D)$ is the value of A_5 if there is no mixing with A^* and thus $\langle\varphi(AD)|r|\varphi(A_pD)\rangle$ and $\langle\varphi(AD)|r|\varphi(A_\alpha D)\rangle$ do not contribute, and $A_5(A^*D)$ is the value of A_5 if only mixing with A^* contributes. For all the systems studied a very large percentage of A_5 is due to mixing with the locally excited state of the acceptor and with $\langle\varphi(A^-D^+)|r|\varphi(A^-D^+)\rangle$. Mixing with the excited amine and with $\langle\varphi(AD)|r|\varphi(A^-D^+)\rangle$ contributes to a much smaller extent.

TABLE 6

The fluorescence rate constant

	$A_5(AD)$ (s ⁻¹)	$A_5(AD^*)$ (s ⁻¹)	$A_5(A^-D^+)$ (s ⁻¹)	$A_5(-A^*D)$ (s ⁻¹)	$A_5(A^*D)$ (s ⁻¹)	A_5 (s ⁻¹)
1N2NM	5.4×10^7	8.3×10^4	2.8×10^5	5.4×10^7	1.1×10^7	3.0×10^7
2N2NM	1.1×10^7	3.8×10^3	4.7×10^4	1.1×10^7	1.7×10^7	1.2×10^7
1N3NM	3.3×10^7	2.6×10^4	1.8×10^5	3.1×10^7	3.6×10^6	2.4×10^7
2N3NM	1.9×10^6	5.0×10^3	7.9×10^4	1.6×10^6	1.6×10^7	1.3×10^7

3.5. Influence of the solvent

The results are summarized in Table 7. The solvents used are hexane ($\epsilon = 1.9$), dibutyl ether ($\epsilon = 3.0$), diethyl ether ($\epsilon = 4.3$), tetrahydrofuran ($\epsilon = 7.6$) and acetonitrile ($\epsilon = 37.5$). A cavity radius ρ of 4.7 Å was used for the ethane systems, and $\rho = 4.8$ Å was used for the propane systems. The experimental data are for piperidine as donor [27].

It can be concluded from Table 7 that, for all the systems studied, the emission wavelength increases with increasing ϵ , k_F drops slightly with increasing ϵ and the percentage CT increases and the percentage $A_\alpha D$ diminishes with increasing ϵ . This can be explained by the fact that a more polar solvent stabilizes the CT state more, thereby producing a bathochromic shift. This induces a larger percentage CT. A larger difference between non-polar and polar solvents is observed for the 2-substituted system because their CT character is more influenced by solvent polarity.

TABLE 7
Influence of the solvent

	ϵ	λ_{calc} (nm)	λ_{exp} (nm)	k_{F} (s ⁻¹)	CT(ex) (%)	$A_{\alpha}D(\text{ex})$ (%)
1N2NM	1.9	348	≈ 360	3.0×10^7	92.2	1.7
	3.0	379	≈ 390	2.8×10^7	94.1	1.0
	4.3	400	≈ 430	2.6×10^7	94.1	0.8
	7.6	426		2.4×10^7	96.0	0.8
	37.5	460	≈ 490	2.2×10^7	96.0	0.5
2N2NM	1.9	332	≈ 345	1.2×10^7	29.2	67.2
	3.0	350	≈ 350	1.5×10^7	44.9	51.8
	4.3	382		1.6×10^7	67.2	29.2
	7.6	423	≈ 430	1.5×10^7	81.0	16.0
	37.5	480	≈ 480	1.3×10^7	86.5	9.6
1N3NM	1.9	394	≈ 395	2.4×10^7	92.2	4.4
	3.0	416		2.2×10^7	92.2	3.6
	4.3	431	≈ 427	2.1×10^7	92.2	3.2
	7.6	449	≈ 446	1.9×10^7	94.1	2.9
	37.5	471		1.8×10^7	94.1	2.6
2N3NM	1.9	387	≈ 395	1.3×10^7	84.6	8.4
	3.0	417		8.7×10^6	86.5	6.3
	4.3	438	≈ 427	6.9×10^6	88.4	5.3
	7.6	468	≈ 446	5.3×10^6	90.3	4.4
	37.5	500		3.8×10^6	90.3	4.0

A plot of $\bar{\nu}_{\text{max}}$ as a function of

$$f - \frac{1}{2}f' = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1}$$

for the ethane systems yields a straight line for the 1-naphthyl compounds. A deviation from linearity is observed for the 2-naphthyl compounds in solvents of low polarity. In non-polar media the exciplex is stabilized to a large extent by the locally excited state, whereas a more marked CT contribution is present in polar media. A linear dependence is observed for systems with a propane chain and the percentage CT does not change drastically.

4. Experimental details

1N2NM and 2N2NM were synthesized by reacting dimethylamine with the corresponding ω -naphthylethylbromide. 1N3NM and 2N3NM were obtained by reducing the amides derived from the acid chloride and the amine. The acid chloride was synthesized by reacting the corresponding naphthylmethyl chloride with diethylmalonate followed by decarboxylation

and formation of the acid chloride. The products were identified using nuclear magnetic resonance, UV, IR and mass spectroscopy. They were purified by thin-layer chromatography using a mixture of 85% *n*-hexane, 14% tetrahydrofuran and 1% triethylamine as eluents.

All the solvents were purified by means of standard procedures and their spectral properties and purities were checked before use.

The wavelengths of the exciplex emission maxima were determined from corrected fluorescence spectra which were measured using a Fica 55 Spectrofluorimètre Différentiel Absolu and a Spex Fluorolog. 5×10^{-5} M solutions of the compounds were made up in the appropriate solvent and were degassed by the application of four freeze-pump-thaw cycles.

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