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THE ELECTRONIC STRUCTURES OF INTRAMOLECULAR EXCIPLEXES WITH ALIPHATIC AMINES AS DONORS

Part I

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ABSTRACT

Intramolecular exciplex formation between tertiary aliphatic amines and a phenyl group is investigated. The influences of the aliphatic chain length and para substitution of the phenyl moiety on the exciplex properties (fluorescence, rate constant, formation rate constant) are determined. The results are qualitatively linked to the relative contributions from the charge-transfer and the locally excited states of the exciplex. The splitting of the degeneracy of the phenyl LUMO by the positive charge on the nitrogen atom is also demonstrated.

INTRODUCTION

Inter- and intra-molecular exciplex formation between an aromatic amine donor and an aromatic acceptor has been extensively studied from both the experimental [1, 2] and the theoretical [3] points of view. However, less data [4—6] are available concerning exciplexes formed between an aromatic acceptor and an aliphatic amine. Linking the donor and acceptor [7] by an alkyl chain severely limits the translational and rotational freedom of both chromophores. Introduction of substituents (—CN, —F) on the *para* position of the phenyl nucleus destroys the degeneracy of the phenyl LUMO and influences the donor—acceptor interactions in the complex. Varying the chain length, the phenyl substitution or the solvent polarity changes the overlap or the relative energies of the charge-transfer and locally excited states. These changes are reflected in a difference in the mixing between the charge-transfer state and the ground or locally excited states. The experimental values of the exciplex emission energy, the dipole moment and the fluorescence rate constant yield a qualitative measure of this mixing which will be compared in a subsequent paper with a theoretical model, isomorphous to that developed by Beens and Weller [3], for exciplexes with aromatic donors.

EXPERIMENTAL

Materials

2-(4-Cyanophenyl)-1-*N*,*N*-dimethylaminoethane (CNP2NM) and 3-(4-cyanophenyl)-1-*N*,*N*-dimethylaminopropane (CNP3NM) were obtained from Professor A. Gilbert and purified by TLC on alumina with diethyl ether/isopentane as eluant immediately before preparation of the solutions. *p*-Fluorotoluene (PFT) and *p*-cyanotoluene (PCNT) were obtained from Aldrich and Suchardt respectively. Prior to use they were purified by TLC on silica with hexane as eluant. 2-(4-Fluorophenyl)-1-*N*,*N*-dimethylaminoethane (FP2NM) was prepared from 4-fluorophenylacetic acid by the standard method [9]. The compound was purified by TLC on alumina with ether/isopentane as eluant. [NMR data: δ 6.7 (m), 4H, phenyl protons; 2.5 (m), 4H, ethane system (AP'BB'); 2.2 (s), 6H, methyl groups. Mass spectroscopy showed peaks due to $M^{+\cdot}$ and $CH_2N(CH_3)_2{}^+$].

3-(4-Fluorophenyl)-1-*N*,*N*-dimethylaminopropane (FP3NM) was synthesized from 4-fluoroacetophenone. Dimethylammonium chloride (16.8 g), *p*-formaldehyde (6.3 g) and *p*-fluoroacetophenone (30 g) were refluxed for 2 h in ethanol (25 ml). After addition of acetone (200 ml) and cooling, a white crystalline solid was obtained, 2-(4-fluorobenzoyl)-1-*N*,*N*-dimethylaminoethane hydrochloride. A sample of the hydrochloride (4 g) was added to a suspension of $LiAlH_4$ (3.8 g) in THF (90 ml) and refluxed for 4 h. After removal of the excess $LiAlH_4$ by ethyl acetate and addition of water, the organic layer was extracted with $CHCl_3$. Evaporation of $CHCl_3$ yielded a yellow oil which was identified as 3-*N*,*N*-dimethylamino-1(-4-fluorophenyl)-propan-1-ol [NMR data: δ 7.1 (m), 4H, phenyl protons; 5.7 (bs), 1H, HO; 4.9 (t), 1H, $-CH$; 2.5 (m), 2H, $-CH_2-N$; 2.2 (s), 6H, CH_3-N; 1.75 (m), 2H, $C-CH_2-C$].

A small quantity of this alcohol (4 g) was then refluxed with 48% HBr (12 ml) for 1 h. The excess acid and water were evaporated off and the product extracted with diethyl ether, after neutralization of the remaining acid by $NaHCO_3$. After evaporation of the ether, a yellow oil, 1-(4-fluorophenyl)-3-*N*,*N*-dimethylaminopropene, was obtained [NMR data: δ 2.4 (m), 4H, phenyl protons; 6.45 (d), 1H, $\phi-CH=-$; 5 (m), 1H, $=CH-$; 3.05 (d), 2H, CH_2-N; 2.2 (s), 6H, CH_3-N].

The olefin was reduced by hydrogen in methanol using Pd on carbon as catalyst [NMR data: δ 0.9 (m), 4H, phenyl protons; 2.7 (t), 2H, $\phi-CH_2$; 2.1 (t), 2H, CH_2-N; 2.1 (s), 1H, CH_3-N; 1.75 (m), 2H, $C-CH_2-C$. Mass: 181.1289 $M^{+\cdot}$].

Isopentane (Merck, Krasol) was used without further purification.

Methods

Emission spectra were recorded on a "Fica Spectrofluorimètre absolu et différentiel". Fluorescence decay was observed by a single photon-counting technique. The observed decay was fitted to a one- or two-exponential decay convoluted with the flash lamp profile by minimizing the sum of the weighted squares of the residuals [10].

RESULTS

Fluorescence spectra in isopentane

p-*Fluorotoluene and* p-*cyanotoluene*

The emission spectra of *p*-fluorotoluene (PFT) and *p*-cyanotoluene (PCNT) are shown in Fig. 1. Decreasing the temperature from 25 to —100°C causes the intensity of the emission to increase; no other emission appears.

FP2NM, CNP2NM and CNP3NM

The emission spectra of CNP2NM, CNP3NM and FP2NM in isopentane at room temperature, normalized at the maximum, are shown in Fig. 2. On decreasing the temperature, the emission spectra of the bichromophoric sys-

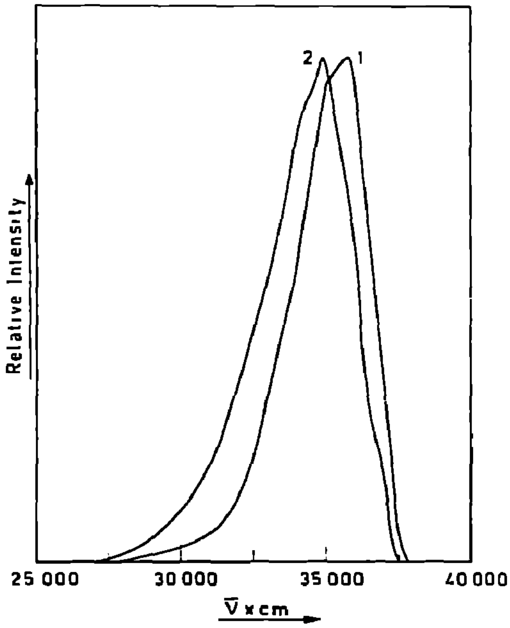


Fig. 1. Emission spectra of the model compounds normalized at the maximum: (1) PFT; (2) PCNT.

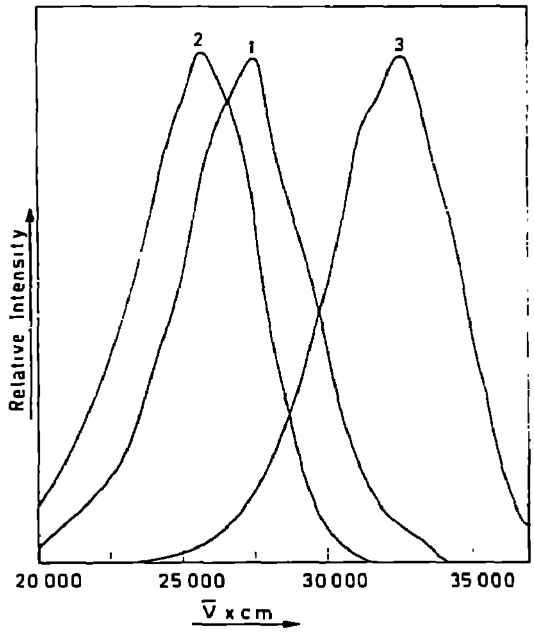


Fig. 2. Emission spectra of FP2NM, CNP2NM and CNP3NM at room temperature in isopentane. All spectra are normalized at the maximum: (1) CNP2NM; (2) CNP3NM; (3) FP2NM.

tems exhibit a slight bathochromic shift (invariably less than 10 nm). Even at −100°C no emission from the locally excited state is observed for FP2NM, CNP2NM and CNP3NM. Assuming that all quenching of the locally excited state leads to exciplex formation [11], it follows that the quantum yields of the exciplex are equal to one at all temperatures.

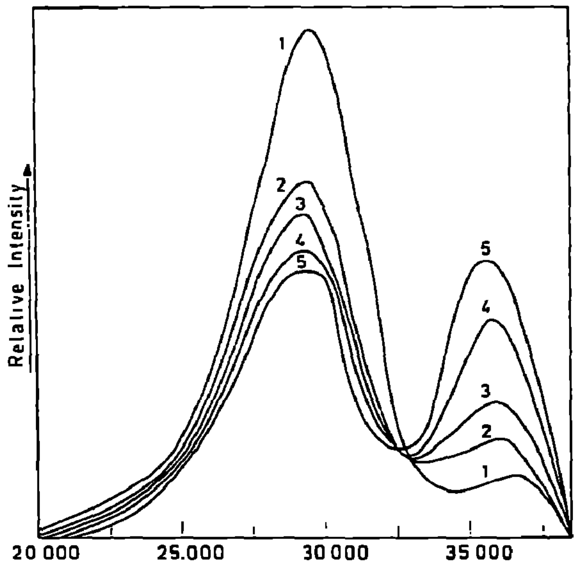
FP3NM

The emission spectrum of FP3NM in isopentane at room temperature consists of a band with a maximum at 29 680 cm^{-1} (338 nm). On lowering the temperature, the intensity of this emission band decreases and a second band at the position of that of PFT is observed (Fig. 3). A plot of $\ln(\phi_E/\phi_{LE})$ against temperature is shown in Fig. 4 and indicates that in the temperature range studied exciplex formation is kinetically controlled.

Fluorescence decay measurements

Both model compounds PFT and PCNT decay exponentially (Fig. 3) at all temperatures. Lowering the temperature causes the singlet lifetime to increase (Fig. 5).

The emission of the exciplex of FP2NM, CNP2NM and CNP3NM decays exponentially between room temperature and −130°C. This is consistent with the fact that exciplex formation is fast compared to the time resolution of the apparatus and that the quantum yield of exciplex formation is equal



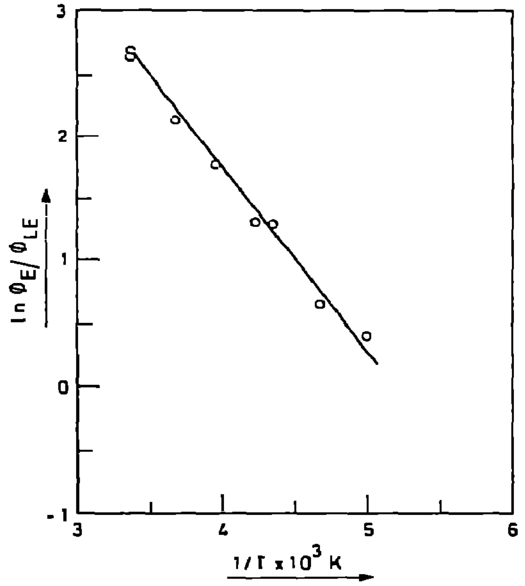
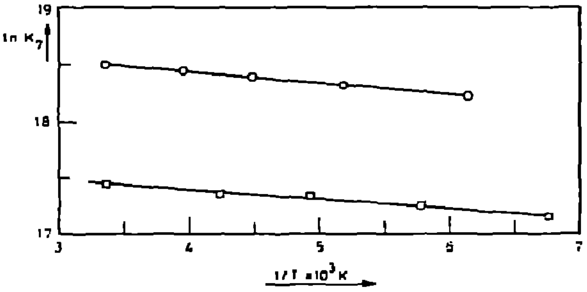


Fig. 3. Emission spectra of FP3NM in isopentane at various temperatures: (1) 23; (2) −20; (3) −42; (4) −58; (5) −72°C.

Fig. 4. Influence of temperature on $\ln(\phi_E/\phi_{2E})$ for FP3NM in isopentane.



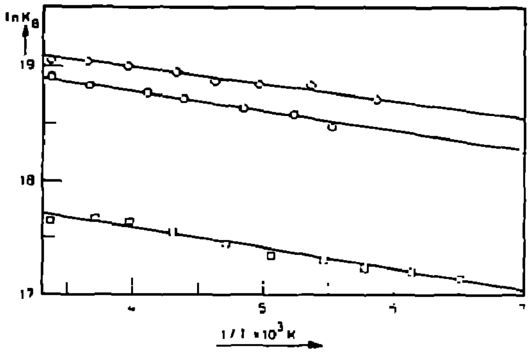


Fig. 5. Influence of temperature on the lifetimes of the model compounds: PFT (○); PCNT (□).

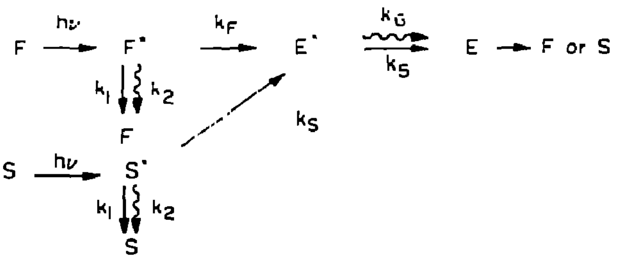
Fig. 6. Influence of temperature on ln k_8 : FP2NM (○); CNP2NM (◇); CNP3NM (□).

to one at all temperatures. As can be seen from Fig. 6, the lifetime of the exciplex k_8^{-1} as defined in Scheme 1 increases with a decrease in temperature.

The exciplex emission of PF3NM decays exponentially above −40°C. Below −40°C the decay of this emission can be considered as a difference between two exponentials.

The emission of the locally excited state decays as the sum of two exponentials. The fast decay corresponds within experimental error to the appearance of the exciplex. The slow decay at lower temperatures corresponds to the decay of PFT and that of the exciplex and occurs over a shorter time interval than both decay processes at higher temperatures.

Similar results were obtained for 2-phenyl-1-*N*,*N*-dimethylaminoethane (P2NM), 3-phenyl-1-*N*,*N*-dimethylaminopropane (P3NM) and 4-phenyl-1-*N*,*N*-dimethylaminobutane (P4NM) in isopentane. The slow decay component of the emission of the locally excited state was due to conformations for which exciplex formation is slow [11]. For FP3NM the same kinetic scheme as that proposed for P2NM, P3NM and P4NM can be used. (Scheme 1.)



Scheme 1

In this scheme $k_7 = k_1 + k_2$, $k_8 = k_5 + k_6$, F and F* are the ground and excited states respectively of a conformation for which exciplex formation is fast, S and S* are the ground and excited states respectively of a conformation for which exciplex formation is slow, E and E* are the ground and lowest singlet state of the exciplex.

The fluorescence decay processes of the locally excited state, $I_{LE}(t)$, and of the exciplex, $I_E(t)$, are represented by eqns. (1) and (2) respectively

$$I_{LE}(t) \simeq f_F \exp-(k_F + k_7)t + f_S \exp-(k_S + k_7)t \tag{1}$$

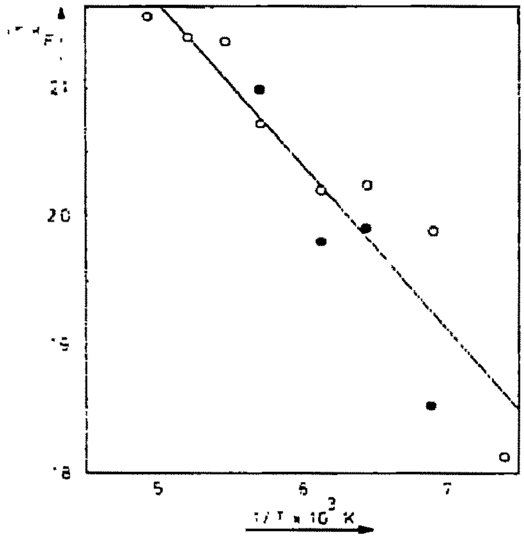
$$I_E(t) \simeq \left(\frac{f_S k_S}{k_8 - k_S}\right) \exp-(k_S + k_7)t + \left(\frac{f_F k_F}{k_8 - k_F}\right) \exp-(k_7 + k_F)t - \left(\frac{f_F k_F}{k_8 - k_F} + \frac{f_S k_S}{k_8 - k_S}\right) \exp(-k_8 t) \tag{2}$$

where f_F and f_S denote the fractions of the molecules in the "fast" and the "slow" conformations respectively.

When k_S and k_F are much larger than k_7 eqn. (2) simplifies to

$$I_E(t) \simeq \exp(-k_8 t) \tag{3}$$

From the temperature dependence of k_F, the preexponential factor, A_F, and the activation energy, E_F, can be obtained (Fig. 7).



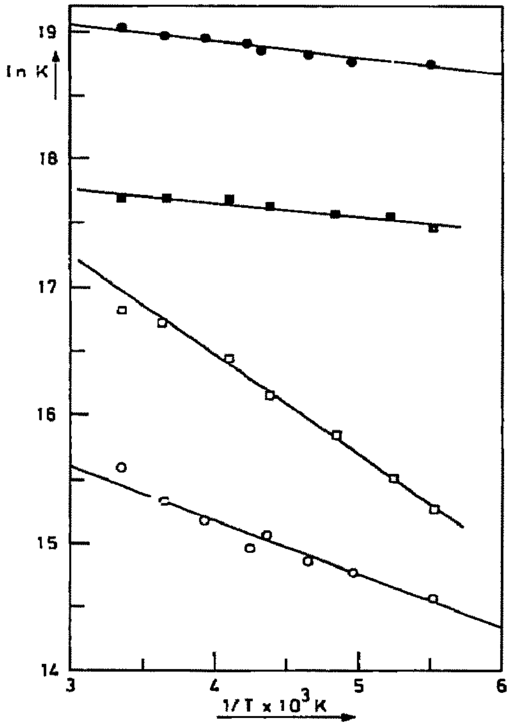


Fig. 7. Influence of temperature on k_f and for FP3NM: determined from λ_2^{290} (○); determined for λ_2^{340} (●).

Fig. 8. Influence of temperature on k_5 and k_6 for the fluoro compounds: k_5, $n = 2$ (□); k_6, $n = 2$ (■); k_5, $n = 3$ (○); k_6, $n = 3$ (●).

The values of k_S are small differences between two large numbers ($\lambda_S = k_S + k_7$ and k_7) and are therefore not accurate enough to allow determination of A_S and E_S.

Determination of k$_5$ *and* k$_6$

The quantum yield of exciplex emission is given by

$$\phi_E = \frac{k_5}{k_8}\left(\frac{k_F f_F}{k_7 + k_F} + \frac{f_S k_S}{k_7 + k_S}\right) = \frac{k_5}{k_8}\,\phi_E^{\text{for}} \tag{4}$$

For CNP2NM, CNP3NM and FP2NM, ϕ_E^{for} is equal to one at all temperatures. For FP3NM, ϕ_E^{for} can be calculated from the decay of the emission of the locally excited state. This leads to k_5 from

$$k_5 = \phi_E\, k_8 / \phi_E^{\text{for}} \tag{5}$$

The values of k_5 obtained in this way are temperature dependent. The pre-exponential factor A_5 and the activation energy E_5 can be determined (Table 1) from an Arrhenius plot. The value of k_6 is now calculable as the difference between k_8 and k_5. An Arrhenius plot of k_6 allows the determination of A_6 and E_6 (Figs. 8 and 9).

DISCUSSION

Formation of the exciplex

For FP2NM, CNP2NM and CNP3NM it was not possible to determine the rate of formation of the exciplex. This implies that for these compounds exciplex formation is much faster than for the corresponding compounds without a *para* substituent on the phenyl group. A possible explanation for this is that dipole—dipole interactions between the amine dipole and that of

TABLE 1

Values of the activation energy (kJ mol^{-1}) and preexponential factor (s^{-1})

	P2NM[c]	FP2NM	CNP2NM	P3NM[c]	FP3NM	CNP3NM
E_F	13.4	a	a	12.8	11	a
E_S	15	a	a	11	a	a
E_5	6[b]	6.5	5	3.8	3.8	3.5
E_6	—	1.1	0	0.5	1	0
A_F	4.6×10^{12}	a	a	6×10^{11}	2×10^{12}	a
A_S	3.1×10^{10}	a	a	7.5×10^{9}	a	a
A_5	2.8×10^{8}[b]	3.2×10^{8}	3.2×10^{8}	7×10^{7}	2.4×10^{7}	9.2×10^{7}
A_6	—	2.2×10^{8}	1.5×10^{8}	7×10^{7}	4.8×10^{8}	2.7×10^{7}
k_1 (s^{-1})	3.4×10^{6}	1.4×10^{7}	4.6×10^{6}	3.4×10^{6}	4.4×10^{7}	4.6×10^{6}

[a] Could not be determined (see text). [b] Determined in THF (for P3NM no difference between THF and isopentane is observed for A_5 and E_5). [c] From ref. 11a.

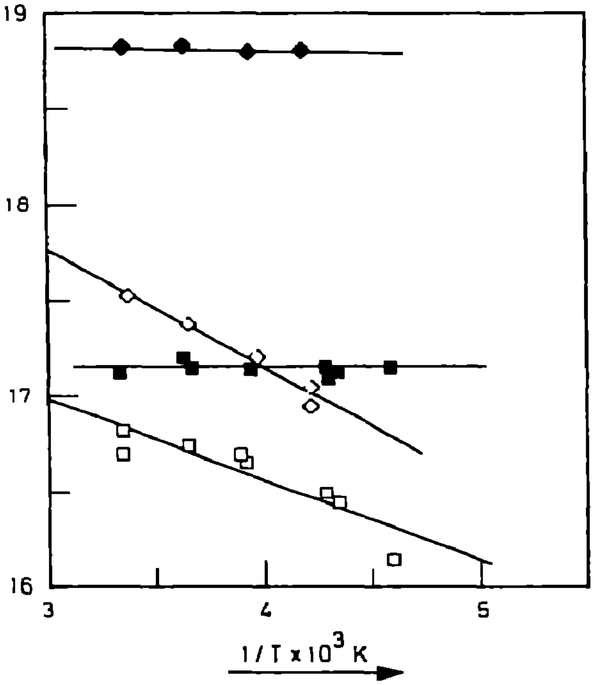


Fig. 9. Influence of temperature on k_5 and k_6 for the cyano compounds. k_5, n = 2 (◇), k_6, n = 2 (◆); k_5, n = 3 (□) k_6, n = 3 (■).

the *para* substituent, or more importantly bond interactions, favour the folded (eclipsed or g±g∓) conformations. Another explanation is that exciplex formation is slower than it would be if it was diffusion controlled in the case of the unsubstituted compounds. Due to the less negative reduction potential of the phenyl nucleus following the introduction of the *para* substituent, the rate of exciplex formation from the encounter conformation [11b] increases. This should then increase the total rate of exciplex formation. A study of the ground-state conformational equilibrium presently underway is hoped to resolve this problem.

k_5

For compounds with the same chain length, the same value for E_5 is obtained. Within experimental error the same also holds for A_5. Thus it may be concluded that the borrowing of oscillator strength from the $S_1 \rightarrow S_0$ transition of the amine or from the L_b transition of the phenyl group does not contribute significantly to A_5. The mixing with these states changes when the energy of the CT state is lowered by 0.5 eV [12] following the introduction of the cyano group. In benzene the LUMO becomes degenerate [8]. In the case of the exciplex, the LUMO is expected to be that linear combination of the two benzene LUMO's for which the Coulomb attraction is a maximum. Introduction of a *para* substituent also destroys this degeneracy. An electron-withdrawing group (CN) stabilizes the LUMO with b_{1u}

symmetry while an electron-donating substituent (F) stabilizes the LUMO with a_u symmetry. These two types of LUMO have different overlaps with the nitrogen *p*-orbital. For the ethane system, where the exciplex is expected to have the eclipsed geometry, the overlap with the a_u orbital is zero while that with the b_{1u} orbital is significant. Nevertheless, for CNP2NM, P2NM and FP2NM similar values for A_5 are observed which suggests that in the ethane system the exciplex LUMO will always be of the same symmetry, probably b_{1u}. This type of LUMO will also have maximum Coulomb attraction. Therefore it may be concluded that the radical cation is at least as important as the *para* substituent in determining the contribution of the b_{1u} or the a_u orbital to the exciplex LUMO.

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