

Exciplex Formation in Complexes between Cyclophane Hosts and Aromatic Guests: Evidence That the Ground-State Complexes Exist in More Than One Distinct Geometry

David R. Benson,^{*,1} Jiaying Fu, Carey K. Johnson, Steven W. Pauls,[†] and David A. Williamson

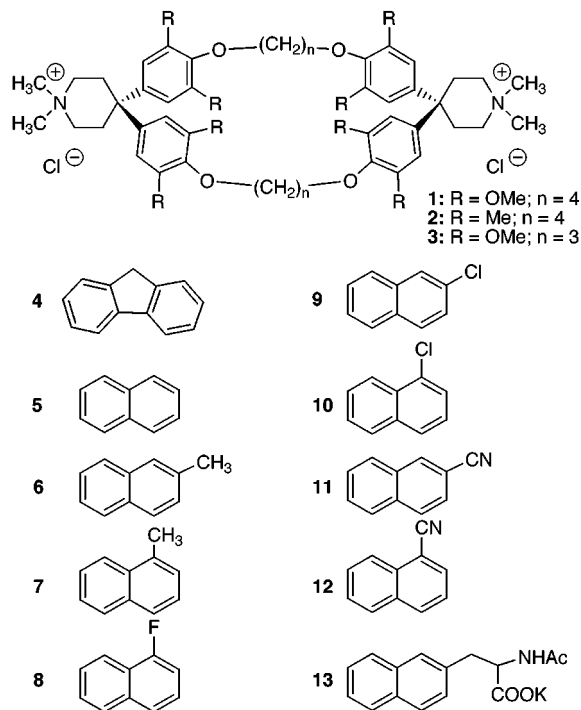
Department of Chemistry University of Kansas Lawrence, Kansas 66045-0046

Received August 26, 1998

Several naphthalene derivatives and fluorene form exciplexes with cyclophane **1** when the host–guest complexes are photoexcited. The electron-rich aromatic units of host **1** act as electron donors (D), while the aromatic guests serve as electron acceptors (A). A linear dependence between exciplex fluorescence energy ($h\nu_e^{\max}$) and the difference between the oxidation potential of the host and the reduction potential of the guest ($E_D^{\text{ox}} - E_A^{\text{red}}$) has been established for the exciplexes observed with fluorene, naphthalene, and 1-fluoronaphthalene, in accord with data from previous studies in which triethylamine is the donor with these and other aromatic acceptors. Points for *N*-acetyl-2-naphthylalanine, 1-methylnaphthalene, 1-chloronaphthalene, and 2-chloronaphthalene deviate from the line, indicating reduced exciplex stability resulting from unfavorable steric interactions between host and guest. The guests with the highest reduction potentials, 1- and 2-cyanonaphthalene, exhibit extensive fluorescence quenching with little or no observable exciplex fluorescence, suggesting efficient formation of solvent-separated radical-ion pairs. Time-resolved fluorescence experiments reveal that the exciplexes arise via two independent pathways, one of which occurs very rapidly. The data indicate that the ground-state host–guest complexes exist at equilibrium in at least two distinct geometries.

Introduction

We recently reported² that host–guest complexes between naphthalene derivatives and **1** in water form exciplexes³ when the complexed guest is photoexcited. The present report focuses on studies between cyclophanes **1** and **2** and a series of aromatic guests (**4–13**) having a range of reduction potentials spanning 670 mV. We find that exciplex fluorescence energy is dependent on guest reduction potential, as previously shown for many other exciplexes,⁴ but that steric interactions between host and guest significantly influence exciplex stability. For guests with high reduction potentials (e.g., **11** and **12**) generation of solvent-separated radical ion pairs competes effectively with exciplex formation. Time-resolved fluorescence experiments demonstrate that the host–guest complexes exist in at least two different geometries in the ground state. In one of these geometries, exciplex formation occurs in less than 20 ps following photoexcitation, whereas in the other exciplex formation requires on the order of 500 ps. Similar findings have been previously reported for intermolecular exciplexes formed between triethylamine (Et₃N) and naphthalene derivatives.^{5,6}



[†] Present address: Department of Chemistry, Centre College, Danville, Kentucky 40422

(1) To whom correspondence should be addressed. Phone: 785-864-4090. Fax: 785-864-5396. E-mail: dbenson@CaCO3.chem.ukans.edu.

(2) Benson, D. R.; Fu, J. *Tetrahedron Lett.* **1996**, *37*, 4833–4836.

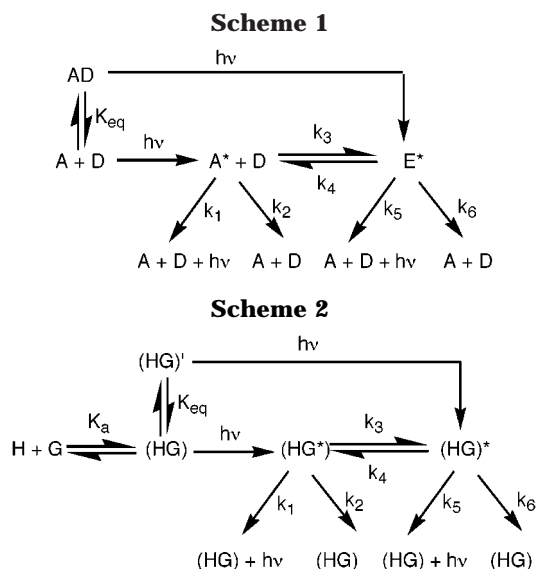
(3) (a) Förster, T. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic: New York, 1975. (b) Mattes, S. L.; Farid, S. *Science* **1984**, *226*, 917–921.

(4) (a) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 839. (b) Rehm, D.; Weller, A. *Z. Phys. Chem. N. F.* **1970**, *69*, 183. (c) Mataga, N.; Ezumi, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1355. (d) Weller, A. in ref 3, pp 23–36.

Efficient intermolecular exciplex formation requires relatively high concentrations of one or both participating compounds, as an excited monomer must encounter a ground-state partner by diffusion (Scheme 1). In Scheme

(5) Biczók, L.; Bérces, T.; Márta, F. *J. Photochem. Photobiol. A* **1989**, *48*, 265–276.

(6) O'Connor, D. V.; Chewter, L.; Phillips, D. *J. Phys. Chem.* **1982**, *86*, 3400–3404.



1, k_1 and k_5 are the rate constants for radiative decay of monomer and exciplex fluorescence, respectively, while k_2 and k_6 are rate constants for all other processes that lead to excited-state decay of monomer and exciplex. Rate constants for exciplex formation and dissociation are k_3 and k_4 , respectively. The equilibrium constant K_{eq} is important in cases where preassociation of A and D to form a ground-state complex (AD) leads to extremely rapid exciplex formation upon photoexcitation.^{5,6}

To circumvent the concentration problem, many studies of exciplexes have centered on covalently linked donor/acceptor pairs that form intramolecular exciplexes.⁷ However, electron transfer from donor to acceptor can occur through the σ bonds of the linkers, thereby increasing the complexity of the system.⁸ Also, the ability of a linked donor/acceptor pair to form an exciplex is dependent on the length and conformational properties of the linkers.⁹

The host-guest exciplexes, even though they are formally *intermolecular*, form from 1:1 complexes that are held together by strong ground-state interactions. Because the excited guest need not encounter a donor group by diffusion, we predicted that excitation of a bound guest would lead to very rapid exciplex formation. However, time-resolved fluorescence studies indicate that the host exists in at least two different geometries (HG) and (HG)', each of which can form the exciplex (Scheme 2). The term K_{eq} in Scheme 2 represents the equilibrium between these two forms. The terms k_1 – k_6 are the same as in Scheme 1, while K_a represents the association constant for host-guest complex formation. H, G, (HG), and (HG)* correspond to host, guest, host-guest complex, and host-guest exciplex, respectively. The host-guest complex in which the complexed guest is excited is represented as (HG*).

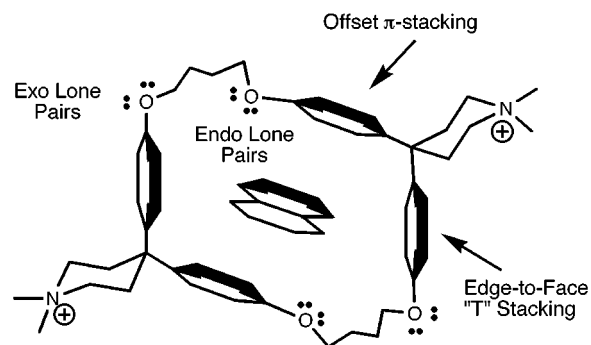


Figure 1. Schematic diagram of host **1** in the geometry reported to be most favorable for binding of guests.

Cyclophanes **1**–**3**, which have been the focus of extensive studies by Diederich and co-workers,¹⁰ form strong ground-state complexes with naphthalene derivatives in polar solvents. The X-ray crystal structure of **3** with no guest bound shows that two oxygen atoms from the $-\text{O}(\text{CH}_2)_3\text{O}-$ linkers have their lone pairs directed toward the inside of the ring (the endo lone pair orientation) while the lone pairs of the others are directed outward (the exo lone pair orientation) (Figure 1).¹¹ The endo-oriented oxygens are directly opposite one another in the cyclophane (i.e., each diphenylmethane unit has one endo oxygen), as are the exo oxygens. The CH_2 groups attached to the oxygen atoms with exo lone pairs are pointed inward, whereas those attached to the oxygen atoms with endo lone pairs are directed outward. An extensive conformational search using Monte Carlo statistical mechanics methods has suggested that the orientations described above are maintained in the complex with *p*-xylene and other benzene derivatives.¹² The lowest energy geometry calculated for the complex between **3** and *p*-xylene shows that offset π -stacking interactions between host and guest involve the host aromatic rings that have endo-oriented oxygens. This orientation allows for more effective π - π interactions than are possible with the other rings, due to steric barriers introduced by the inward-directed methylene units. The guest engages in T-stacking (edge-to-face) interactions with the other two aromatic rings of the host. Molecular modeling studies with **1** have shown that it can form a related conformation that allows for binding of guest in a similar orientation.

Electronic complementarity between host and guest is an important factor in determining binding strength in organic solvents, with electron-poor guests binding more strongly than electron-rich ones.¹³ However, electron donor-acceptor (EDA) bands were not observed in UV/vis spectra for these complexes.¹³ For binding studies in water, EDA interactions can be masked by solvent effects.¹⁴

The time-dependent decay of monomer (A^*) fluorescence intensity (i_A) and exciplex (E^*) fluorescence inten-

(7) De Schryver, F. C.; Collart, P.; Vandendriessche, J.; Goedeweck, R.; Swinnen, A. M.; Van der Auweraer *Acc. Chem. Res.* **1987**, *20*, 159–166.

(8) (a) De Schryver, F. C.; Declercq, D.; Depaemelaere, S.; Hermans, E.; Onkelinx, A.; Verhoeven, J. W.; Gelan, J. *J. Photochem. Photobiol. A* **1994**, *82*, 171–179. (b) Verhoeven, J. W. *Pure Appl. Chem.* **1990**, *62*, 1585–1596.

(9) (a) Swinnen, A. M.; Van der Auweraer; De Schryver, F. C.; Nakatani, K.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1987**, *109*, 321–330. (b) Zhang, S.-I.; Lang, M. J.; Goodman, S.; Durnell, C.; Fidler, V.; Fleming, G. R.; Yang, N. C. *J. Am. Chem. Soc.* **1996**, *118*, 8, 9042–9051.

(10) Diederich, F. *Cyclophanes*; Royal Society: Cambridge, 1991; Chapters 2 and 3.

(11) Ferguson, S. B.; Seward, E. M.; Diederich, F.; Sanford, E. M.; Chou, A.; Inocencio-Szweda, P.; Knobler, C. B. *J. Org. Chem.* **1988**, *53*, 5595–5596.

(12) (a) Jorgensen, W. L.; Nguyen, T. B.; Sanford, E. M.; Chao, I.; Houk, K. N.; Diederich, F. N. *J. Am. Chem. Soc.* **1992**, *114*, 4003–4004. (b) Jorgensen, W. L.; Nguyen, T. B. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 1194–1200.

(13) Ferguson, S. B.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1127–1129.

(14) Reference 10, p 117.

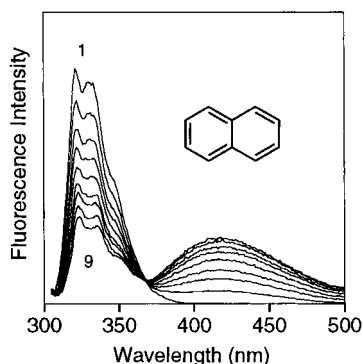


Figure 2. Titration of 14 μM naphthalene (**5**) with **1** in water at 26 $^{\circ}\text{C}$ ($\lambda_{\text{exc}} = 300 \text{ nm}$). Spectrum 1: $[\mathbf{1}] = 0 \mu\text{M}$. Spectrum 9: $[\mathbf{1}] = 590 \mu\text{M}$.

sity (i_{E}) can be described by eqs 1 and 2.^{5,15} In these equations, c_1 – c_4 are constants and λ_1 and λ_2 are decay parameters.¹⁶ Under conditions where the quencher (D) is present in very high concentrations, λ_1 and λ_2 are as defined in eqs 3 and 5, respectively.¹⁵

$$i_{\text{A}}(t) = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t) \quad (1)$$

$$i_{\text{E}}(t) = c_3 \exp(-\lambda_1 t) + c_4 \exp(-\lambda_2 t) \quad (2)$$

$$\lambda_1 = k_1 + k_2 + k_3[\text{D}] + k_4 \quad (3)$$

$$\lambda_{1(\text{HG})} = k_1 + k_2 + k_3' + k_4 \quad (4)$$

$$\lambda_2 = k_4 + k_5 + k_6 \quad (5)$$

Because guest in the host–guest complexes is held in enforced proximity to the donor (D), exciplex formation is essentially a unimolecular process. Thus, the term $k_3[\text{D}]$ in eq 3 can be replaced by k_3' (eq 4). The decay curves for the monomer and for the exciplex will both be biexponential. The preexponential terms c_3 and c_4 in eq 2 should be of equal magnitude but opposite in sign if exciplex formation occurs by a single pathway.^{5,6,15}

Results

Figure 2 shows a titration of naphthalene (**5**) with cyclophane **1** in water at 298 K. As the concentration of **1** increases, the fluorescence intensity of the guest, which is held at constant concentration, decreases markedly. A broad, red-shifted band appears during the titration, suggestive of the presence of an exciplex. Similar results were obtained when **4** (Figure S1, Supporting Information), **8** (Figure S2, Supporting Information), and **9** and **10** (Figure S3, Supporting Information) are examined as guests with **1**, but the exciplex emission maxima ($h\nu_{\text{e}}^{\text{max}}$) vary (Table 1). In titrations of **11** and **12** with **1**, guest fluorescence is strongly quenched. In the titration with **11**, evidence of exciplex formation is provided by an isoemissive point near 490 nm when the spectra are overlaid (Figure 3). No such point is observed in the titration with the more strongly oxidizing **12** (Figure S4, Supporting Information). With 2-methylnaphthalene (**6**) (Figure S5, Supporting Information), 1-methylnaphtha-

lene (**7**) (Figure S6, Supporting Information), and the potassium salt of *N*-acetyl-2-naphthylalanine (**13**) (Figure 4), enhancement of monomer fluorescence occurs upon complexation by **1**. For **6**, emission at long wavelengths is very weak. For the isomeric **7**, an exciplex is in evidence, but it is still rather weak. Finally, for **13** the exciplex signal is much stronger, yet monomer fluorescence enhancement is still observed.

Host **1** absorbs strongly below 295 nm, but has a very weak, tailing absorbance band that extends beyond 350 nm (Figure S7, Supporting Information). A similar tailing band is observed in UV/vis spectra of 1,2,3-trimethoxybenzene (not shown) and likely represents an intramolecular charge-transfer process. All of the guests have relatively weak absorption bands that also extend beyond 300 nm (the spectra of **5** and **1** are shown overlaid in Figure S7, Supporting Information). Excitation of the host–guest complexes at 300 nm maximizes exciplex signal intensity while minimizing interference from the host. However, at high host-to-guest ratios, co-excitation of host and guest is unavoidable. This can lead to errors in binding constants determined by fluorescence spectroscopy (Table 1), especially for weak binders. Nonetheless, the binding data in Table 1 at least provide a reliable ordering of binding strengths for the host–guest complexes. Binding constants for **9** and **10** were not determined due to rapid dechlorination reactions that occur upon photoexcitation.

In the presence of the methyl-substituted host **2**, enhancement of monomer fluorescence is observed for **5**–**10**, with no evidence for exciplex formation except for a weak one with **10** (not shown). Titrations could only be performed over a small range of host concentrations, due to aggregation of the host above 20 μM .¹⁷ Enhancement of monomer fluorescence has previously been reported for binding studies of naphthalene derivatives with related cyclophanes. The fluorescence enhancement results from selective excitation of bound guest, due to red-shifts in the UV spectrum of bound guest relative to guest in aqueous solution.¹⁸ For guest **4**, addition of **2** leads to a decrease in monomer fluorescence intensity. The extinction coefficient of **4** at the exciting wavelength (300 nm) shows a corresponding decrease in the presence of **2** (not shown). With both **11** and **12**, addition of **2** leads to strong quenching of guest fluorescence. With **11** (Figure 5), but not **12** (not shown), a weak exciplex is also in evidence.

Values of $h\nu_{\text{e}}^{\text{max}}$ for a series of exciplexes between triethylamine (Et_3N ; $E_{\text{D}}^{\text{ox}} = +1.1 \text{ V}$ in acetonitrile vs SCE)¹⁹ and **4**–**12** in cyclohexane from a 1978 report by Van and Hammond²⁰ are listed in Table 1. Half-wave reduction potentials for **4**,²¹ **5**,^{19b,21,22} **11**,²³ and **12**²³ in Table 1, all measured by cyclic voltammetry (CV) vs SCE

(17) Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 362.

(18) Diederich, F.; Dick, K. *J. Am. Chem. Soc.* **1984**, *106*, 8024–8036.

(19) (a) Loveland, J. W.; Dimeler, G. R. *Anal. Chem.* **1961**, *33*, 6–1201. (b) Yoon, U. C.; Mariano, P. S.; Givens, R. S.; Atwater B. W., III. *Adv. Electron-Transfer Chem.* **1994**, *4*, 117–205.

(20) Van, S.-P.; Hammond, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3895–3902.

(21) Bock, H.; Lechner-Knoblauch, U. *Z. Naturforsch.* **1985**, *40b*, 1463–1475.

(22) (a) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317–6324. (b) Lewis, F. D.; Zebrowski, B. E.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 187. (c) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Marcel Dekker: New York, 1970; p 41.

(23) McCullough, J. J.; Miller, R. C.; Fung, D.; Wu, W.-S. *J. Am. Chem. Soc.* **1975**, *97*, 5942–5943.

(15) (a) Ware, W. R.; Watt, D.; Holmes, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 7853–7864. (b) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970; Chapter 7.

(16) We assign λ_1 and λ_2 as the parameters defining exciplex formation and decay, respectively, as in refs 5 and 6. Ware et al.^{15a} and Birks^{15b} assign them oppositely.

Table 1. Data for Exciplexes Formed between Compounds 4–13 and Either Et₃N, 1, or 2 and from Binding Titrations of 4–13 with 1

guest	E_A^{red} (eV)	$E_{0,0}$ (eV)	ΔG_{ET}^a (kcal/mol)	$h\nu_e^{\text{max}}$ (Et ₃ N) (eV)	$h\nu_e^{\text{max}}$ (1) (eV)	K_a (M ⁻¹)
4	-2.65	4.19 ^b	-2.1	3.218	3.100	2×10^5
5	-2.50	3.97 ^c	-0.5	3.026	2.960	2.8×10^4
6	-2.50 ^f	3.93 ^c	+0.5	3.042	<i>h</i>	1.3×10^5 (W) 2.8×10^3 (MW)
7	-2.50 ^f	3.94 ^c	+0.2	3.053	3.131	1.6×10^3 (MW)
8	-2.40 ^f	3.95 ^c	-2.3	2.970	2.877	2.3×10^4
9	-2.34 ^f	3.90 ^c	-2.5	2.916	2.897	<i>h</i>
	-2.30 ^g					
10	-2.29 ^f	3.92 ^c	-4.1	2.867	2.831	<i>h</i>
	-2.26 ^g					
11	-2.13	3.76 ^d	-2.5 (1) +1.6 (2)	2.722	<i>i</i>	1.6×10^5
12	-1.98	3.89 ^e	-10.6 (1) -4.8 (2)	2.598	<i>i</i>	2.1×10^4
13	-2.50 ^f	<i>h</i>	<i>h</i>	<i>h</i>	3.047	7.0×10^4

^a For exciplexes with 1, unless otherwise noted. ^b From ref 47. ^c Reference 48. ^d Reference 49. ^e Reference 50. ^f Estimated (see text). ^g Reference 25. ^h Not determined. ⁱ None observed. ^j MW = 3:1 water/methanol; W = water.

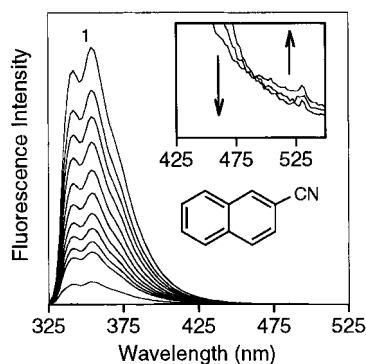


Figure 3. Titration of 20 μM 2-cyanonaphthalene (11) with 1 in water at 26 $^\circ\text{C}$ ($\lambda_{\text{exc}} = 300$ nm). Spectrum 1: [1] = 0 μM . Spectrum 11: [1] = 96 μM .

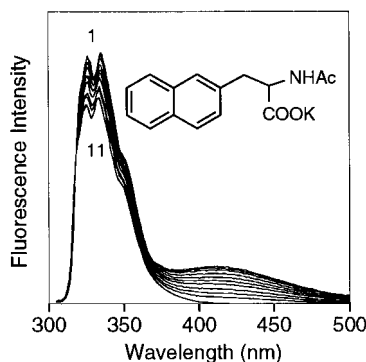


Figure 4. Titration of 50 μM *N*-acetyl-2-naphthylalanine (13) with 1 in water at 26 $^\circ\text{C}$ ($\lambda_{\text{exc}} = 300$ nm). Spectrum 1: [1] = 0 μM . Spectrum 11: [1] = 350 μM .

in dimethylformamide (4 and 5) or acetonitrile (11 and 12), were obtained from the literature. Plotting $E_D^{\text{ox}} - E_A^{\text{red}}$ vs $h\nu_e^{\text{max}}$ for these exciplexes with Et₃N gives a nearly straight line, consistent with expectations from previous literature reports⁴ (Figure 6; Van and Hammond did not report such a plot in their paper). Reduction potentials for 5–7 in aqueous dioxane are very similar²⁴ but are different than those reported for 5 in DMF. We thus used E_A^{red} of -2.50 eV (the value measured for 5 in DMF) for 5–7 and 13. Standard potentials for 9 and 10 were measured by Andrieux et al.²⁵ using the homoge-

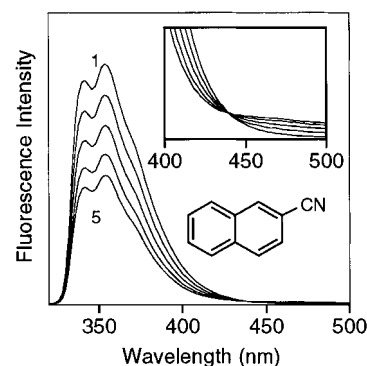


Figure 5. Titration of 20 μM 2-cyanonaphthalene (11) with 2 in water at 26 $^\circ\text{C}$ ($\lambda_{\text{exc}} = 300$ nm). Spectrum 1: [2] = 0 μM . Spectrum 5: [2] = 17 μM .

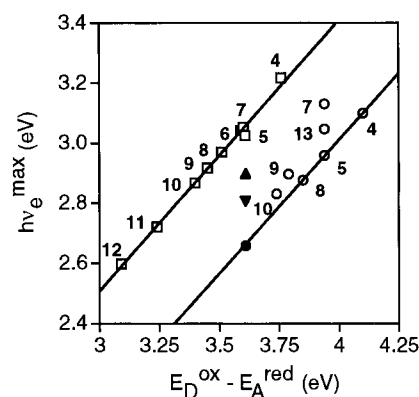


Figure 6. Plots of $E_D^{\text{ox}} - E_A^{\text{red}}$ vs $h\nu_e^{\text{max}}$ for exciplexes between Et₃N and 4–12 in cyclohexane (□) and for exciplexes between 1 and 4–13 in water (○). Also shown are values for the exciplex between Et₃N and naphthalene (5) in dibutyl ether ($E_T(30) = 33.0$) (▲), diethyl ether ($E_T(30) = 34.5$) (▼), and tetrahydrofuran ($E_T(30) = 37.4$) (●).

neous redox catalysis method. CV cannot be used with 9 and 10 because these compounds undergo rapid dechlorination upon reduction to the radical anion.²⁵ When the standard potentials are plotted vs $h\nu_e^{\text{max}}$ from their exciplexes with Et₃N in cyclohexane, their points deviate from the line generated using 4–7, 11, and 12. In addition, reliable reduction potentials for 8 are not

(24) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; pp 272–273.

(25) Andrieux, C. P.; Saveant, J. M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107–116.

Table 2. Data from Time-Resolved Fluorescence Experiments for Complexes between Host 1 and Guests 4, 5, 7 and 8

guest	λ^a (ns ⁻¹)	λ_1 (ns ⁻¹) ($c_3 < 0$)	λ_2 (ns ⁻¹) ($c_4 > 0$)	$ c_4 / c_3 $	$(c_4 - c_3)/ c_3 $
4	0.19	1.81	0.045	1.94	0.49
5	0.027 (0.026) ^b	1.32 <i>c</i>	0.049 (0.041)	3.08 <i>c</i>	0.68 <i>c</i>
7	0.029	1.16	0.031	5.88	0.83
8	0.037	2.22 (3.53)	0.069 (0.057)	1.60 (6.0)	0.38 (0.83)

^a Fluorescence decay of guest in absence of host. ^b Data in parentheses represent measurements performed on degassed samples. ^c Not observed.

available. We thus calculated approximate reduction potentials for **8–10** using the equation for the line defined by **4–7**, **11**, and **12**. We consider this a reasonable approach, as steric interactions between Et₃N and the different acceptors are not expected to cause deviation from the linear behavior expected from previously reported studies.⁴ Assuming linear behavior for all exciplexes with Et₃N also allows us to better evaluate any deviations from linearity observed with the host–guest exciplexes. From this plot we arrive at eq 6 for Van and Hammond's data.²⁰

$$h\nu_e^{\max} = 0.90(E_D^{\text{ox}} - E_A^{\text{red}}) - 0.217 \text{ eV} \quad (6)$$

Also plotted in Figure 6 are data for naphthalene (**5**) in a series of ether solvents of different polarities, taken from Van and Hammond's paper. Polarity is defined in terms of Reichardt's empirical $E_T(30)$ parameter.²⁶ For acetonitrile ($E_T(30) = 45.6 \text{ kcal mol}^{-1}$) and ethanol ($E_T(30) = 51.9 \text{ kcal mol}^{-1}$) absence of exciplex emission was reported with **5**.

Using the reduction potentials of **4–10** either obtained from the literature or predicted, we have plotted $E_D^{\text{ox}} - E_A^{\text{red}}$ vs $h\nu_e^{\max}$ for our host–guest exciplexes in water (Figure 6). For E_D^{ox} in this plot we use the value for 1,2,3-trimethoxybenzene in acetonitrile (+1.45 V vs SCE),²⁷ which serves as a model for the aromatic donor moieties of **1**. The points for **4**, **5**, and **8** define a straight line (eq 7) having a similar slope to the line through Van and Hammond's data, but a larger constant term.

$$h\nu_e^{\max} = 0.89(E_D^{\text{ox}} - E_A^{\text{red}}) - 0.55 \text{ eV} \quad (7)$$

The points for **7**, **9**, **10**, and **13** in the host–guest system are shifted to the blue from the positions predicted using eq 7 (Figure 6).

Time-resolved fluorescence experiments have been performed for the exciplexes between guests **4**, **5**, **7**, and **8** and host **1** (Table 2). The fluorescence decay curve for the exciplex with naphthalene (**5**) is shown in Figure 7. The exciplex decay curves for **4**, **5**, and **7** are biexponential, with a decay term (λ_2) and a formation term (λ_1 ; Table 2). Experiments with **5** demonstrate that these parameters are independent of relative concentrations of host and guest ($[1]/[5]$ varied from 1.4 to 15, with $[5]$ held constant at 50 μM ; data not shown), demonstrating that the rise time does not result from a diffusional process involving electronically excited but uncomplexed guest. For the exciplex with **8**, three exponentials are required to fit the data, one of which is a rise. The shorter

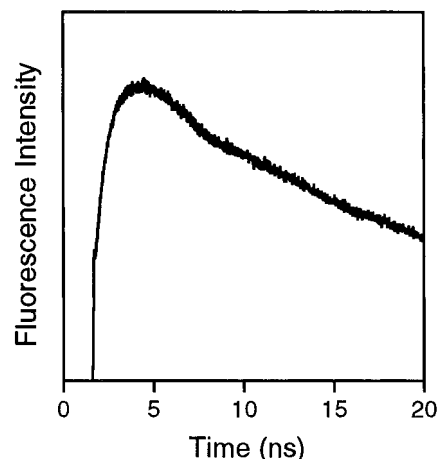


Figure 7. Time-resolved fluorescence emission for the exciplex between **1** and **5**. Excitation is at 300 nm, and emission is at 450 nm.

decay is more than 10-fold faster than the other. As yet, we have no explanation for this faster decay.

Excitation of pure host and of 1,2,3-trimethoxybenzene at 300 nm leads to a weak fluorescence signal that extends beyond 450 nm. To minimize effects from host fluorescence, samples used for most of the time-resolved fluorescence studies (vide infra) were performed with relatively small excesses of host. Time-resolved fluorescence data for **1** ($[1] \approx 300 \mu\text{M}$, $\lambda_{\text{exc}} = 300 \text{ nm}$, $\lambda_{\text{ems}} = 450 \text{ nm}$) reveal a multiexponential decay process (not shown). Fluorescence intensity relative to a sample containing **1** ($\approx 300 \mu\text{M}$) and **5** (50 μM) was negligible.

Oxygen, which initially was not precluded from the samples used for time-resolved studies, is known to quench fluorescence. To determine whether oxygen influences the time-resolved behavior of the host–guest systems, we examined degassed samples of complexes between host **1** and guests **5** and **8**, as well as a sample of **5** alone. Exclusion of oxygen resulted in a 60% increase in λ_1 and a 21% decrease in λ_2 (Table 2) for **8**. Exclusion of O₂ from the complex between **1** and **5** resulted in a fluorescence decay that was monoexponential and in which λ_2 was decreased by ca. 17%. Exclusion of oxygen had a much smaller effect on fluorescence decay of pure **5** in water.

Interestingly, the preexponential factors for the exciplex formation time (c_3) and the exciplex decay time (c_4) are not equal for any of the host–guest exciplexes (Table 2), even though they are expected to be so if the exciplex arises from a single ground-state distribution of donor (host) and acceptor (guest).^{4,5,15} This is true whether oxygen was precluded from the sample or not (see data for **8** in Table 2), although the absence of O₂ led to a substantial increase in c_4 relative to c_3 . The relative values of c_3 and c_4 indicate that some exciplexes are

(26) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1990; Chapter 7.

(27) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124–4129.

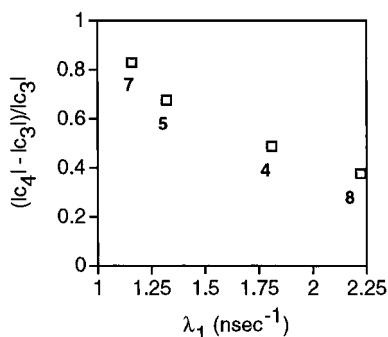


Figure 8. Plot of $(|c_4| - |c_3|)/|c_3|$ vs λ_1 for the exciplexes between host **1** and guests **4**, **5**, **7**, and **8**. Data are reported in Table 2.

formed via a process much more rapid than those that we can observe experimentally.

For situations in which exciplexes form both via diffusional process involving A^* and D and from direct excitation of a ground-state complex (AD) (Scheme 1), plots of $(|c_4| - |c_3|)/|c_3|$ vs $(\lambda_1 - \lambda_2)$ yield information regarding the equilibrium constant (K_{eq}) for formation of AD from A and D .^{4,5} Our results indicate that the host-guest exciplexes form from two different ground-state complexes (Scheme 2). Because exciplex formation in these cases is essentially intramolecular, K_{eq} in the host-guest systems represents the equilibrium constant between two different ground-state host-guest complexes (HG') and (HG), the former generating an exciplex rapidly following photoexcitation, the latter having a higher barrier to exciplex formation (eq 8).

$$(|c_4| - |c_3|)/|c_3| = (\lambda_1 - \lambda_2)[E^*]/[HG^*]k_3' = (\lambda_1 - \lambda_2)\epsilon_{HG'}[(HG)']/[HG]\epsilon_{HG}k_3' \quad (8)$$

In eq 8, ϵ_{HG} and $\epsilon_{HG'}$ are the extinction coefficients for the two different host-guest complexes, respectively, and k_3' is the unimolecular rate constant for exciplex formation. Assuming that $\epsilon_{AD} \approx \epsilon_A$ and ignoring λ_2 , eq 8 can be simplified to

$$(|c_4| - |c_3|)/|c_3| \approx \lambda_1 K_{eq}/k_3' \approx (k_1 + k_2 + k_3' + k_4)K_{eq}/k_3' \quad (9)$$

A plot of $(|c_4| - |c_3|)/|c_3|$ vs λ_1 for **4**, **5**, **7**, and **8** is shown in Figure 8, and values of $(|c_4| - |c_3|)/|c_3|$ are reported in Table 2.

Discussion

Effect of Solvent Polarity and Acceptor Reduction Potentials on Exciplex Fluorescence Energy. Compounds **4–12** form exciplexes with Et_3N in cyclohexane. The exciplex fluorescence energy maxima for these exciplexes plot linearly with $E_D^{ox} - E_A^{red}$ with a slope slightly less than one (eq 6), consistent with previous reports of exciplexes in which the donor is held constant and the acceptor is varied (Figure 6).⁴ Of the same group of aromatic acceptors, all but **12** give evidence for exciplex formation with cyclophane **1** in water. The slope of the line defining the data for exciplexes between **1** and guests **4**, **5**, and **8** is also less than one (eq 7). Points for the other guests deviate from this line for reasons that will be discussed below.

From Figure 6 we see that for a given difference in E_D^{ox} and E_A^{red} the host-guest system yields an exciplex that fluoresces at longer wavelength (lower energy). For example, $E_D^{ox} - E_A^{red}$ for $Et_3N - \mathbf{4}$ (3.76 eV) is nearly the same as for **1–10** (3.74 eV), yet the exciplex fluorescence energies for the two exciplexes differ by 0.39 eV (8.9 kcal mol⁻¹). This difference is due to the high polarity of water relative to cyclohexane, which results in stabilization of the exciplex charge-transfer state.²⁸

The fluorescence energy for the exciplex between Et_3N and **5** in tetrahydrofuran ($E_T(30) = 37.4$) falls on the line defined by eq 7 for the host-guest exciplex systems (Figure 6). If eq 7 adequately describes exciplexes in which Et_3N is the donor rather than the host, this would suggest that the solvation experienced by the two exciplex components is significantly less polar than water ($E_T(30) = 63.1$ kcal mol⁻¹). Assuming that the guest is deeply buried in the host cavity in both the ground state and excited state complexes, the host-component of the exciplex would be fully exposed to water while the guest component would be in an environment of lower polarity. This would truly reduce the effective solvent polarity experienced by the host-guest exciplexes. Interestingly, $E_T(30)$ values for aromatic ethers such as anisole and 1,2-dimethoxybenzene (which serve as reasonable models for the aromatic rings of the host) are in the range of 37–38 kcal/mol,²⁶ consistent with this explanation.

An alternative explanation for the apparent low polarity of the solvent is that the exciplexes are less stable than what would be predicted on the basis of the host and guest redox potentials. Maximum stabilization of exciplexes formed between two aromatic molecules typically requires that they adopt a "sandwich" arrangement having maximum π overlap.²⁹ Exciplexes having large charge-transfer components are believed to be less constrained to a particular geometry (i.e., they are "loose").⁸ However, we have found that bulky substituents on both the host and the guest significantly reduce exciplex stability (manifested as a blue-shift in the exciplex fluorescence energy), suggesting that close approach of host and guest π -systems is still important even when charge-transfer contributions are large. Complete overlap of the donor and acceptor π systems is not possible in the host-guest complexes, however, due to steric barriers imposed by the structure of the cyclophane.¹⁰ What is achieved is an offset π -stacking arrangement between the guest and two opposing aromatic rings of the host that confers stabilization to the ground-state complex. The inability of the host and guest π -systems to fully overlap will lead to an exciplex that is of lower stability than the corresponding exciplex in which 1,2,3-trimethoxybenzene (a reasonable model system for the host) was the donor. We predict that both of these factors contribute to the apparent low solvent polarity in the host-guest exciplexes.

Influence of Host and Guest Substituents on Exciplex Stability We have found that the points for **9** and **10** are displaced from the line defining the data for **4**, **5**, and **8** (Figure 6). Guests **7** and **13** are displaced to a greater extent, indicating an even larger decrease in

(28) (a) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183–1184. (b) Weller, A. *Z. Phys. Chem. N. F.* **1982**, *133*, 93–98.

(29) (a) Haenel, M. W.; Lintner, B.; Benn, R.; Rufinska, A.; Schroth, G.; Krüger, C.; Hirsch, S.; Irngartinger, H.; Schweitzer, D. *Chem. Ber.* **1985**, *118*, 4884. (b) Lintner, B.; Schweitzer, D.; Benn, R.; Rufinska, A.; Haenel, M. W. *Chem. Ber.* **1985**, *118*, 4907.

exciplex stability (the exciplex signal for **6** could not be resolved due to overlap with the strong monomer fluorescence). These guests differ from the others in having bulky substituents attached to the aromatic nucleus. Alkyl groups on benzene have similarly been shown to reduce the stability of excimers.³⁰ The larger blue-shifts for **7** and **13** relative to **9** and **10** suggest greater contribution of exciton resonance in their host–guest exciplexes, consistent with their lower reduction potentials (Table 1). In addition, methyl groups are about 15% larger than chlorine atoms,³¹ and the substituent in **13** is larger yet. Steric effects with these guests should therefore be more pronounced. Note, however, that the exciplex with **13** is more stable than the exciplex with **6**, contrary to what might be expected on the basis of the relative sizes of the substituents.

In the exciplexes between host **1** and guests **6**, **7**, and **13** (Figures S5 and S6, Supporting Information, and Figure 4, respectively), both monomer fluorescence enhancement and exciplex formation are observed to occur. This suggests that these exciplexes (E^*) are, at best, only modestly stabilized relative to complexed, electronically excited monomer (HG^*). Furthermore, the extent of monomer fluorescence enhancement is inversely related to the exciplex fluorescence intensity. These exciplexes are similar in stability (based on exciplex fluorescence energies, Figure 6) to the exciplex between Et_3N and the naphthalene (**5**) in cyclohexane. Two groups of researchers have previously reported that this same exciplex is only weakly stabilized and that its main mode of decay is dissociation back to Et_3N and excited naphthalene (k_4 in Scheme 1).^{4,32} For naphthalene derivatives having electron-withdrawing substituents (e.g., **12**), exciplex formation with Et_3N is reported to be irreversible.^{4,5}

Although the substituent on **13** is much larger than the methyl groups on **6** and **7**, **13** forms a much stronger exciplex. Furthermore, **7** forms a stronger exciplex than **6**. These observations suggest that the three guests adopt different ground-state binding geometries, which to a greater or lesser extent interfere with exciplex formation. We predict that **13** will be oriented such that its polar substituent is maximally exposed to water. For **6** and **7**, in contrast, the substituted ring will be free to enter the host cavity.

In molecular dynamics studies with cyclophane **3**, it was found that benzene preferred an orientation in which it was not deeply buried in the host cavity.¹² Rather, the benzene ring is “clasped by the four methoxy methyl groups on one side of the host”, an interaction that is energetically favorable due to the partial positive charges on the methyl group hydrogens and the partial negative charges on the aromatic carbons.¹² A similar kind of arrangement can be envisaged for **6** and **7**, wherein the unsubstituted ring of the guest interacts preferentially with the methoxy methyl groups on one side of the host, while the ring bearing the methyl group is inserted in the host cavity, interacting favorably with the host aromatic rings. Such a binding geometry would greatly reduce π – π interactions between host and guest, thereby interfering with exciplex formation. With the more substituted ring of **13** pulled further out of the cavity,

favorable interactions between the methoxy methyl groups and that ring are still possible. The unsubstituted ring will thus be within the cavity, making exciplex formation more favorable. The stronger exciplex formation with **7** than with **6** suggests that these guests have different orientations within the host cavity as well. CPK model investigations suggest that the ring bearing the substituent in **7** cannot penetrate the host cavity as deeply as its unsubstituted ring or the 2-substituted ring of **6**. Thus, **7** should experience less steric hindrance to exciplex formation than **6**.

The influence of steric interactions on host–guest exciplex stability is also manifested in different behaviors of hosts **1** and **2**. The oxidation potential of **2** is about 250 mV higher than that for **1** (i.e., it is more difficult to oxidize), based on the reported oxidation potential of 2,4,6-trimethylanisole (+1.70 V),³³ a suitable model for **2**. Thus, for a given guest, an exciplex formed with host **2** will be less stable by about 5.7 kcal/mol. Host **1** forms an exciplex with fluorene (**4**), which has a reduction potential of -2.65 V. The reduction potential of 1-fluoronaphthalene (**8**) is 250 mV lower (-2.40 V). Thus, a host–guest exciplex between **2** and **8** should be similar in stability to the exciplex between **1** and **4** (eq 3) barring unfavorable interactions. However, host **2** does not form an exciplex with **8**. The first evidence for exciplex formation is observed with 1-chloronaphthalene (**10**), with a reduction potential (-2.29 mV) that is 360 mV more negative than that for **4**. This exciplex, however, is quite weak, and monomer fluorescence enhancement is also observed (similar to the situation for exciplexes between host **1** and guests **6**, **7**, and **13**). We suggest that the inability of **2** to form exciplexes with most guests results from the greater steric bulk of its methyl substituents relative to the methoxy substituents on **1** (conformational free energies for methyl and methoxy groups on cyclohexane are 1.8 and 0.6 kcal mol⁻¹, respectively). This situation is analogous to the weak exciplex formation observed for the methylnaphthalenes (**6** and **7**) relative to naphthalene (**5**).

Evidence for Two Competing Pathways to Exciplex Formation. Host–guest exciplexes form from excited-state acceptor molecules that are already pre-associated with a donor. This provides a situation in which exciplex formation is essentially intramolecular, so that exciplex formation rates as high as 10^{12} s⁻¹ or larger become possible.³⁴ However, time-resolved fluorescence studies have revealed that some fraction of each host–guest exciplex requires hundreds of picoseconds to form. For all exciplexes examined, the preexponential terms describing exciplex formation and decay are unequal ($|c_4| > |c_3|$) (Table 2). This points toward a situation in which at least two distinct populations of host–guest complexes exist at equilibrium, each of which forms an exciplex but with dramatically different rates. A similar situation has been reported before for exciplexes between Et_3N and naphthalene derivatives bearing electron-withdrawing substituents.^{4,5} The dual pathway was attributed to a preassociation of some population of the molecules to form a ground-state complex, which upon excitation produced the exciplex with no formation time (Scheme 1).

(30) Birks, J. B.; Braga, C. L.; Lumb, M. D. *Proc. R. Soc. London, Ser. A* **1965**, *283*, 83–99.

(31) Meyer, A. Y. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1567–1572.

(32) Meeus, F.; Van der Auweraer, M.; De Schryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4017–4024.

(33) Hammerich, O.; Parker, V. D.; Ronlan, A. *Acta Chem. Scand. B* **1976**, *30*, 89–90.

(34) Peters, K. S. *Adv. Electron-Transfer Chem.* **1994**, *4*, 27–52.

The concentration-dependence study performed with the naphthalene exciplex shows convincingly that the rise time does not result from a diffusional process involving excited, unbound guest. In other words, exciplex formation only occurs with guests that are already complexed by a host. A simple equilibrium distribution of guests with differences in orientation relative to the host cavity does not satisfactorily explain the observations either, as such a distribution would lead to a formation time descriptive of the entire ensemble. Thus, the results point toward a situation in which two or more distinct populations of host–guest complexes exist at equilibrium, separated by energy barriers. Photoexcitation of this equilibrium mixture leads to exciplexes that form at different rates.

When oxygen was excluded from the complex between **1** and **8**, a decrease in λ_2 was recorded. There were concomitant increases in the values of λ_1 and of $(|c_4| - |c_3|)/|c_3|$ (Table 2). For the complex between **1** and **5** in the absence of O₂, decay was monoexponential and λ_2 was again observed to decrease. In contrast, there was only a minor increase in fluorescence lifetime for **5** (with no host present) when O₂ was excluded from solution. Because the guest in the host–guest complexes is protected against contact with O₂, the effect of O₂ on complexed guest will be even less significant.³⁵ The effectiveness of oxygen at quenching exciplex fluorescence indicates that eq 5 should be rewritten as eq 10 for the samples containing O₂.

$$\lambda_2 = k_4 + k_5 + k_6 + k_7[\text{O}_2] \quad (10)$$

Quenching of exciplex fluorescence by oxygen will decrease the amount of exciplex that is able to dissociate. Thus, k_4 will decrease in the presence of O₂, leading to lower values of both λ_1 (eq 4; Table 2) and $(|c_4| - |c_3|)/|c_3|$ (eq 9; Table 2), as observed. As exciplex formation becomes less favorable (i.e., with **5** relative to **8**), the values of c_4 may become so large relative to c_3 that a rise time is not observable in time-resolved experiments when O₂ is absent from the sample. This is apparently the situation we have encountered for the complex between **1** and **5** (Table 2). Thus, inclusion of O₂ ultimately was beneficial in that it permitted observation of slow exciplex formation processes for all of the host–guest complexes in this study.

Possible Explanations for Two Different Host–Guest Binding Geometries. We suggest two scenarios to explain the presence of host–guest complexes having more than one distinct geometry. The first scenario rests upon the assumption that the host is always in the form represented in Figure 1. In this scenario, the guest can bind in one of two orientations separated by an energy barrier: (1) deep within the host cavity, engaging in aromatic–aromatic interactions of the type previously reported to be responsible for the strong binding observed with this class of receptors (vide supra), or (2) interacting preferentially with the methoxy methyl groups of the host, which requires that the guest be less deeply buried in the host cavity. This scenario is supported by findings with guests **6**, **7**, and **13**, whose abilities to form exci-

plexes depend on the size and placement of their substituents. They are also supported by calculations suggesting that benzene complexed by host **3** prefers to interact with the methoxy methyl groups of the host, rather than engaging in aromatic–aromatic interactions with the aromatic walls of the host. In this scenario, the fraction of host–guest complexes in which the guest is deeply buried in the host cavity will form exciplexes more rapidly, a result of much greater overlap of host and guest π -systems. The other segment of bound guest molecules will need to change their orientation following excitation in order to form the exciplex, resulting in a formation time.

The second possibility is that the host exists in two or more conformational ensembles, each of which binds guest efficiently, but not all of which have sufficient electronic coupling between donor and acceptor to permit extremely rapid exciplex formation (the term conformational ensemble indicates that while the ArOCH₂ units are fixed, other bonds in the molecule can still freely rotate). Again, the fraction of complexes forming exciplexes rapidly would have the guest deeply buried in the host having the geometry represented in Figure 1 (host conformational ensemble A).

This scenario is based upon CPK model studies, which indicate that the host can adopt two other conformational ensembles in which the cavity is sufficiently large to accommodate naphthalene-sized guests. These have either (B) a single endo lone pair or (C) four exo-oriented lone pairs. These can interconvert in two ways: (1) rotation about the appropriate Ar–O bond, which based upon studies of 1,2-dimethoxybenzene should have a barrier on the order of 3 kcal/mol³⁵ or (2) rotation about the C–C bond between the aromatic ring and the piperidinyll moiety. Although we do not have an estimate for the latter rotation barrier, it would necessarily require that no guest be bound in the cavity and can thus be safely ignored for the present discussion.

The inward directed methylene units in C would prevent van der Waals contact between host and guest π -systems, whereas in A and B such contact would be possible with two rings or one ring, respectively. Thus, both A and B could permit rapid exciplex formation due to strong electronic coupling between host and guest. Conformational ensemble C, however, would require at least one C–O bond rotation to occur before an exciplex could form.

An exo orientation for the oxygen lone pairs would permit solvation by water, whereas when directed endo they will encounter the hydrophobic face of the bound guest. Furthermore, freedom of rotation about these bonds (which can readily occur while the guest remains in the cavity) would be favorable in terms of the entropy of the complex. Finally, as noted above, computational studies have suggested that interactions between the methoxy methyl groups of the host and the π -systems of certain guests are stabilizing.¹² Similar stabilizing interactions can also be envisaged between bound guests and the inward-directed OCH₂ groups of B and C.

Relationship between ΔG_{ET} and Exciplex Formation. If $E_{\text{D}}^{\text{ox}} - E_{\text{A}}^{\text{red}}$ for a donor/acceptor pair is smaller than the singlet excitation energy ($E_{0,0}$) of the acceptor,

(35) (a) Diederich, F.; Dick, K.; Griebel, D. *J. Am. Chem. Soc.* **1986**, *108*, 2273–2286. (b) DaKorte, A.; Langois, R.; Cantor, C. R. *Biopolymers* **1980**, *19*, 1281–1288.

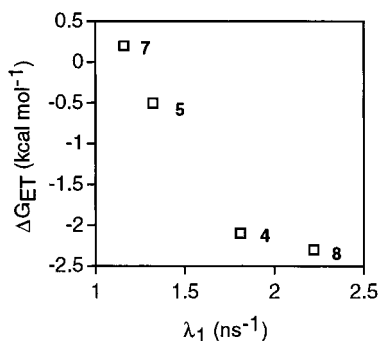


Figure 9. Plot of ΔG_{ET} vs λ_1 for the exciplexes between host **1** and guests **4**, **5**, **7**, and **8**. Data are reported in Table 2.

electron transfer will be exergonic (eq 11).³⁶ Rehm and

$$\Delta G_{ET} = E_D^{ox} - E_A^{red} - E_{0,0} \quad (11)$$

Weller have reported that for $\Delta G_{ET} < -10$ kcal mol⁻¹, electron transfer occurs at a diffusion-controlled rate (ca. 2×10^{10} s⁻¹) in polar solvents such as acetonitrile.³⁶ For isoergonic electron-transfer processes ($\Delta G_{ET} = 0$), rates of 10^9 s⁻¹ are observed. For all donor-acceptor pairs in which $\Delta G_{ET} < +5$ kcal mol⁻¹, outer-sphere electron transfer in acetonitrile leads to formation of solvent-separated radical ion pairs (SSRIPs). Values of $E_{0,0}$ and of ΔG_{ET} for the host-guest complexes with **1** are listed in Table 1 (data are also shown for the complexes of guests **11** and **12** with host **2**). The data indicate that electron transfer will be exergonic in all of the complexes in which **1** is the host, although for most complexes the driving force for this electron transfer will be fairly small.

In the host-guest complexes, photoinduced electron transfer would lead directly to contact radical ion pairs (CRIPs), as host and guest are not initially separated by solvent molecules (a CRIP can be considered as an exciplex in which CT is complete).³⁷ Electron transfer in contact donor/acceptor pairs is several orders of magnitude faster (up to 10^{12} s⁻¹) than in geminate (solvent-separated) D/A pairs, due to enhanced electronic coupling between D and A.^{34,37}

Plotting ΔG_{ET} vs λ_1 (the parameter describing exciplex formation) for the slow exciplex-forming complexes involving **4**, **5**, **7**, and **8** gives a reasonably straight line (Figure 9). Because λ_1 will be dominated by k_3 (the rate of exciplex formation), this demonstrates that the rate of exciplex (CRIP) formation increases as electron-transfer becomes more exergonic, as expected from electron-transfer theory.³⁸ It is interesting to note that the rates of exciplex formation are not necessarily related to exciplex stability, as determined from $h\nu_c^{max}$. For example, exciplex stabilities decrease in the order **8** > **5** > **4**, while formation times increase in the order **8** < **4** < **5**. This reflects the much higher excitation energy of **4** relative to the other two guests (Table 1).

Assuming that the λ_1 value measured for **8** in the absence of O₂ represents a reasonable lower limit for k_3 ($k_3 \gg k_1$ and k_2), we can calculate that rates of exciplex formation are $\geq 3.6 \times 10^9$ s⁻¹ for the guests used in this study. These rates are only about a factor of 2–3 lower

than those calculated for contact electron transfer from alkylbenzene donors to tetracyanoanthracene in acetonitrile when ΔG_{ET} is close to zero.^{34,37b} This suggests that electronic coupling between donor and acceptor in the slow host-guest exciplex-forming fraction is similar to that used in the reported calculations,^{37b} indicating that even in the slow exciplex-forming fraction there is close contact between host and guest. Close contact is consistent with both of the scenarios discussed in the preceding section.

Using the Eyring equation and a value of $\nu = kT/h = 6$ ps⁻¹, ΔG^\ddagger will be ≥ 4.3 kcal mol⁻¹ at 295 K for exciplex formation in the complex between **1** and **8** (using λ_1 as a lower limit for k_3). This estimated energy barrier for exciplex formation is higher than ΔG^\ddagger reported for rotation about the Ar–O bond in 1,2-dimethoxybenzene in the direction which takes the methyl group past the neighboring methoxy group³⁹ (ca. 3 kcal mol⁻¹; $\tau = 1/k \approx 27$ ps at 295 K). Thus, the Ar–OCH₂ bonds could potentially rotate multiple times following guest excitation, consistent with the possible operation of scenario (2) discussed in the preceding section.

The value of $(|c_4| - |c_3|)/|c_3|$ (Table 2) is found to be inversely related to λ_1 (Figure 8) and to ΔG_{ET} (not shown). This suggests either that (1) as exciplex formation becomes less favorable, other processes which comprise λ_1 (eq 4) can compete, or (2) K_{eq} in eq 9 depends on ΔG_{ET} . If (2) is correct, the fraction of fast-forming exciplexes would increase as ΔG_{ET} becomes less negative. This is not a satisfying conclusion, as ΔG_{ET} depends on $E_{0,0}$ of the guest, whereas K_{eq} defines the equilibrium between ground-state host-guest complexes. The other possibility is more likely, as there are processes that can compete with exciplex formation (e.g., k_2 in eqs 4 and 9 and Scheme 2). One such process is energy transfer,⁴⁰ the possible importance of which is supported by overlap between the guest fluorescence spectra and the tailing absorption band of the host (see data for **5** in Figure S7, Supporting Information).

Formation of Radical Ion Pairs Following Photoexcitation. If the solvent is sufficiently polar, CRIPs (exciplexes) can separate to yield SSRIPs.^{34,37} The binding titration between **1** and **11** (Figure 2) showed evidence for a very small amount of exciplex with extensive quenching of monomer fluorescence, suggesting that this host-guest pair may be near the limit at which exciplex (CRIP) formation can compete with generation of SSRIPs. The strongest driving force for electron transfer is for the complex between **1** and **12**. Neither this complex nor the one between **2** and **12** gives evidence for exciplex formation, suggesting exclusive formation of SSRIPs following electron transfer. It is interesting to note that ΔG_{ET} for the complex between **1** and **10** is similar to that for the complex between **1** and **11** (Table 1). However, a much stronger exciplex is observed for the complex with **10**. This is likely due to the higher reduction potential of **11**, which will allow it to form a more stable solvated radical anion. Finally, λ_2 for the exciplex between **1** and **8** is greater than for the exciplex between **1** and **5** (Table 2). Likewise, the fluorescence intensity for the exciplex between **1** and **8** is lower. The higher reduction potential of **8** will result in an exciplex having greater CT contri-

(36) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

(37) (a) Gould, I. R.; Farid, S.; Young, R. H. *J. Photochem. Photobiol. A* **1992**, *65*, 133–147. (b) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068–2080.

(38) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622–630.

(39) Kenschin, H. *J. Mol. Struct.* **1988**, *168*, 293–307

(40) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC: Boca Raton, 1991; pp 168–181.

butions. This should lead to enhanced generation of SSRIPs with a concomitant reduction in exciplex fluorescence intensity and lifetime.

Exergonic electron transfer is also predicted for all guests in the Van and Hammond study.²⁰ For example, ΔG_{ET} for the exciplex between Et_3N and **5** should be -0.36 eV (-8.3 kcal mol⁻¹). However, the low polarity of cyclohexane would favor formation of an exciplex (CRIP) rather than of a SSRIP in all cases. This would most commonly occur via outer-sphere electron transfer followed by collapse to the exciplex in a process referred to as harpooning.⁸ However, as noted above, direct excitation of ground-state EDA complexes can also lead to exciplex formation.^{4,5} Both acetonitrile and ethanol are polar enough to stabilize free-radical ions, and in these solvents no exciplex was formed between **5** and Et_3N indicating generation of SSRIPs in Van and Hammond's study.²⁰

Summary and Conclusion

Host-guest exciplexes are formed upon photoexcitation of several naphthalene derivatives and fluorene confined within the cavity of **1**. Bulky substituents on both host and guest reduce exciplex stability, suggesting the importance of close contact between donor and acceptor π -systems in stabilizing these exciplexes. In the case of **6**, **7**, and **13**, this destabilization leads to formation of host-guest exciplexes that appear to be in equilibrium with complexed, excited monomer. For the electron-deficient guests **11** and **12**, direct electron transfer from host to excited guest to generate radical ion pairs competes effectively with exciplex formation with both **1** and **2**.

Differences in preexponential factors for exciplex formation and decay determined from time-resolved fluorescence experiments reveal that there is more than one pathway to exciplex formation. This indicates that the ground-state host-guest complexes exist in more than one distinct geometry. One pathway is rapid (as predicted based on the enforced proximity of donor and acceptor groups in the ground-state complex), whereas the other requires several hundred picoseconds and depends on the driving force for electron transfer from host to excited guest. Two scenarios have been presented as possible explanations for the different populations of host-guest complexes. We are currently studying the various host-guest complexes via molecular dynamics simulations in order to better understand their behavior in the ground state.

Experimental Section

General Methods. Cyclophanes **1**⁴¹ and **2**,⁴² 1-chloronaphthalene (**10**),⁴³ and 1-cyanonaphthalene (**12**)⁴⁴ were prepared via literature methods. 1-Methylnaphthalene was purified from technical-grade material by HPLC on a 1.0 cm C18 reversed-phase column using H_2O/CH_3CN (1:1) as eluent. All other guests were reagent grade and were used as received. Nanopure water was employed as the solvent in all cases. Guest solutions in H_2O were prepared by 1000-fold dilution of a concentrated stock solution in MeOH, followed by soni-

cation if necessary. Fluorescence spectra were recorded on a Photon Technology International (PTI) QuantaMaster luminescence spectrometer. All samples were thermostated at 26 °C using a circulating water bath. Binding studies were performed by adding aliquots of a host stock solution (ca. 2.5 mM) to a solution of the appropriate guest (ca. 50 μ M) in a quartz cuvette and recording the change in monomer or exciplex fluorescence. To keep the guest concentration constant, the host stock solution contained the same guest concentration as the sample in the cuvette. Association constants (K_a) and free energies of binding ($-\Delta G^\circ$) were determined from nonlinear regression analysis of the binding data.⁴⁵

Time-Resolved Fluorescence Spectroscopy. The fluorescence excitation pulse was produced by a Rhodamine 590 dye laser synchronously pumped by the second harmonic from a Coherent Antares Nd:YAG laser. The repetition rate of the pulse from the dye laser was adjusted to 3.975 MHz using a cavity dumper before being routed to the sample cell. This routinely provided a dye laser pulse with an average power of 250 mW and a half-width of ca. 5 ps. These pulses were then frequency-doubled using a BBO crystal to provide an excitation pulse at a wavelength of 300 nm. The excitation beam was focused into a 1.0 cm \times 1.0 cm quartz sample cell using a 10 cm lens. The focal point of the beam was kept near the front face of the sample cell to prevent reabsorption in the sample. The fluorescence was then collected in a right angle configuration by an off-axis ellipsoidal mirror (Janos Technology). The fluorescence emission was passed through a polarizer set at the magic angle (54.7°) to prevent polarization effects and then scrambled and focused into a small double holographic monochromator (American Holographic; DB-10). The selected emission was focused onto the entire active area of a chilled MCP photomultiplier tube (RU5906), providing two to three counts per second (cps) in the dark.

Fluorescence emission was processed using a time-correlated single photon counting (TCSCP) instrument consisting of a constant-fraction discriminator (CFD), time-to-amplitude converter (TAC), and multichannel analyzer. The TCSCP instrument was operated in reverse mode⁴⁶ to improve the efficiency of collection. An instrumental response function (IRF) was collected with each fluorescence lifetime curve to be used as part of the data fitting procedure. This IRF was used to monitor the scattering of the excitation pulse in the instrument and was collected from a dilute solution of nondairy creamer. Collection in this manner gave an observed IRF on the order of 20 ps. All time-resolved fluorescence decay curves were collected to a minimum of 10 000 counts in the peak channel. The decay curves were analyzed using a fitting program called NEWLIFE, generously shared by Dr. Gary Holtom. These lifetime decays were fit to the function

$$K(t) = \sum a_i \exp(-t/\tau_i) \quad i = 1-4$$

Fitting parameters were optimized using a nonlinear least-squares procedure using the Levenberg-Marquardt algorithm with iterative convolution. The quality of the fit was judged by analyzing the reduced χ^2 value defined by

$$\chi^2_\nu = \sum [I_o(t) - K(t)]^2 / \nu \sigma_i^2$$

where σ is the standard deviation and ν is the number of degrees of freedom.

(45) Associate V. 1.6: Peterson, B. Ph.D. Thesis, University of California at Los Angeles, 1994.

(46) O'Connor, D. V.; Phillips, D. *Time Correlated Single Photon Counting*; Academic: London, 1984.

(47) Auty, A. R.; Jones, A. C.; Phillips, D. *Chem. Phys.* **1986**, *103*, 163-182.

(48) Jacobson, B. A.; Guest, J. A.; Novak, F. A.; Rice, S. A. *J. Chem. Phys.* **1987**, *87*, 269-283.

(49) Reference 24, p 32.

(50) Berden, G.; Meerts, W. L.; Kreiner, W. *Chem. Phys.* **1993**, *174*, 247-253.

(41) Ferguson, S. B.; Sanford, E. M.; Seward, E. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 5410-5419.

(42) Diederich, F.; Dick, K.; Griebel, D. *Chem. Ber.* **1985**, *118*, 3588-3619.

(43) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99-107.

(44) Olah, G. A.; Keumi, T. *Synthesis* **1979**, 112-113.

Acknowledgment. This work was supported by National Science Foundation EPSCoR Grant OSR-9255223 with matching support from the State of Kansas. We thank Prof. Richard S. Givens for helpful discussions and a critical reading of the manuscript.

Supporting Information Available: Fluorescence spectra for complexes between host **1** and guests **4**, **6–10**, and **12**. UV/vis and fluorescence spectroscopic data for **1** and **5** (4 pages). See any current masthead page for ordering information. JO981755F