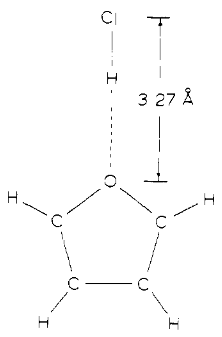

Figure 1. Structure of the furan–HCl complex. The complex is planar.

significantly affect the reported oxygen–chlorine distance.

The rather short oxygen chlorine distance of 3.27 Å and small value observed for D_J indicate strong binding between furan and HCl. If the H–Cl distance were to remain at the free molecule value of 1.3 Å, the O- - -H hydrogen bond length would be 1.97 Å. The corresponding distance is 2.3 Å for benzene–HCl.[7] The structure of the complex is shown in Figure 1. The observed hydrogen bond length of 1.97 Å is significantly longer than the calculated value[1] of 1.783 Å. Molecular orbital calculations do not appear to give as accurate structures for complexes as for the free molecules. The fact that the observed A rotational constant of 9499 MHz for the complex is very close to the A rotational constant of 9447 MHz for free furan strongly suggests the C_{2v} structure shown in Figure 1 with the HCl along the a axis. We have obtained data on the DCl and $H^{37}Cl$ isotopic species, and these data also support the structure given. Work is continuing on this project.

Acknowledgment. The partial support of the National Science Foundation is gratefully acknowledged. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors thank Peter Beak for helpful discussions on this work.

Registry No. Furan, 110-00-9; HCl, 7647-01-0.

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Intramolecular Exciplexes of Polychromophoric Molecules[1]

James R. Larson, Jacob W. Petrich, and Nien-chu C. Yang*

Department of Chemistry, University of Chicago
Chicago, Illinois 60637

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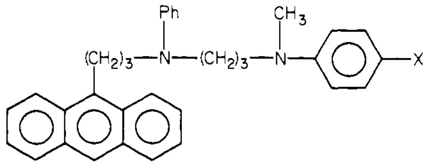
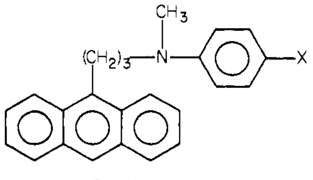
Photoexcited aromatic hydrocarbons form exciplexes with a variety of donors and acceptors.[2] Exciplexes of order higher than 2 are also known which may play important roles in photochemical reactions.[3–12] Light-induced electron transfer in molecular complexes of multiple components has been implicated as the primary step in photosynthesis.[13] However, properties of excited molecular complexes and exciplexes of higher order remained substantially uncharacterized, particularly the role of such complexes in charge transfer.[14] So that the formation and decay of such exciplexes could be probed, polychromophoric molecules of general structures **1** and **2** were synthesized and their spectroscopic properties examined. We concluded that intramolecular ternary exciplexes were formed from **1** under certain experimental conditions, and we were able to determine the factors governing their formation and decay.



1a, X = H
1b, X = OCH_3
1c, X = CH_3



2a, X = H
2b, X = OCH_3

Compounds **1a–c** were synthesized by a conventional method.[15] Compounds **2a,b** were obtained by known routes.[16] Fluorescence spectra of these compounds were measured with a Perkin-Elmer MPF-4 spectrofluorimeter equipped with an electronic corrected spectrum unit and a thermostatic sample compartment, and fluorescence lifetimes were determined via the time-correlated single-photon-counting technique with an apparatus described elsewhere.[17] The fluorescence data are listed in the Table I.

Charge-transfer interaction between components in exciplexes plays an important role in both their stability and decay.[18–20] In solvents of low to medium polarity, this interaction may be analyzed quantitatively by the dependence of fluorescence maximum on the solvent polarity according to the following equation:

$$\tilde{\nu}_{ex} = \tilde{\nu}_{ex}(0) - (\mu_{ex}^2/hca^3)(f - \tfrac{1}{2}f') \qquad (1)$$

where $\tilde{\nu}_{ex}$ is the fluorescence maximum of the exciplex in a given solvent (in cm^{-1}), $\tilde{\nu}_{ex}(0)$ is the maximum in vacuo, μ_{ex} is the dipole

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(1) Dedicated to Professor George H. Büchi on the occasion of his 60th birthday.

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(14) The triple exciplex formed two molecules of naphthalene and one of dicyanobenzene has been well characterized, but this excited state complex has not been suggested to be an intermediate in a photochemical reaction. See ref 3 and 7.

(15) Compounds were synthesized by conventional chemical methods and characterized by elemental and spectroscopic analyses. The procedures are available as a part of the supplementary material.

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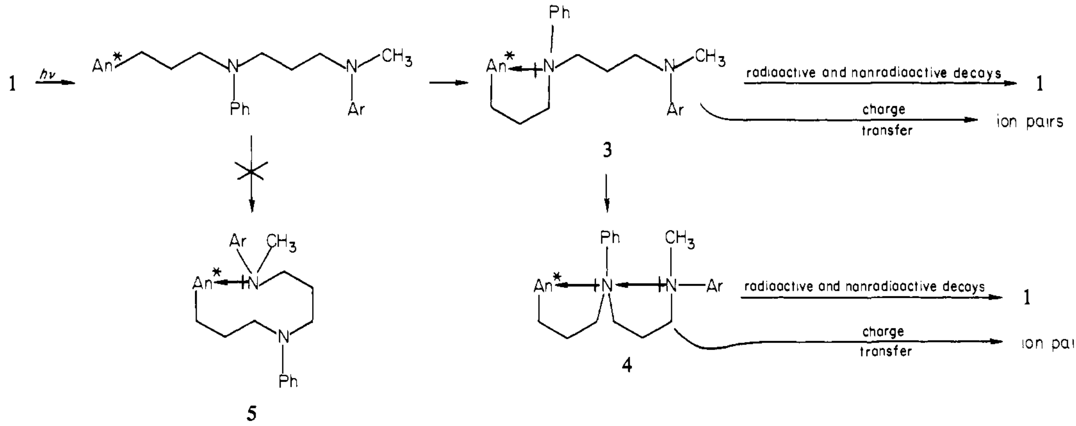
Table I. Exciplex Fluorescence of Polychromophoric Molecules 1 and 2

	compound													
	1a			**1b**			**1c**			**2a**			**2b**	
solvents ($f - {}^1/_2f'$)	$\bar{\nu}_{max}$[a]	ϕ_f[b]	τ[c]	$\bar{\nu}_{max}$[a]	ϕ_f[b]	τ[c]	$\bar{\nu}_{max}$[a]	ϕ_f[b]	τ[c]	$\bar{\nu}_{max}$[a]	ϕ_f[b]	τ[c]	$\bar{\nu}_{max}$[a]	ϕ_f[b]
pentane (0.090)	20.5_3	0.44	80	19.9_6	0.13	59	20.5_3	0.44	82	20.6_2	0.46	79	18.9_7	0.31
methylcyclohexane (0.106)	20.4_9			19.9_2			20.5_3			20.5_3			18.8_7	
trichloroethylene (0.197)	20.0_0			18.5_2			19.9_2			19.9_2			17.8_6	
isopropyl ether (0.239)	20.0_8			17.9_5			19.9_8			20.0_0			18.0_2	
ethyl ether (0.256)	19.9_2	0.14	65	17.7_0	0.03		19.6_5	0.14	10, 57[d]	19.9_2	0.47	111	17.7_0	0.04
n-butyl acetate (0.267)	19.3_8	0.09	27	16.9_5	0.004		18.6_9	0.05	39	19.3_1	0.18	54	16.9_5	0.01
tetrahydropyran (0.276)	19.4_2						18.5_9			19.3_1				
ethyl acetate (0.293)	19.0_5	0.045		16.5_0	<0.004		18.1_8	0.036		19.0_5	0.15		16.5_3	<0.01
tetrahydrofuran (0.306)	19.0_5						18.1_8			18.9_4				
dichloromethane (0.319)	18.8_7						17.8_6			18.8_7	0.12			
$2\mu_{ex}^2/hca^3$ (10^{-3} cm^{-1})	−7.0 ± 1.0			−16.5 ± 1.5			−5.2 ± 0.6[e] −15.5 ± 1.3[f]			−7.6 ± 1.0			−10.5 ± 2.1	

[a] In units of 10^3 cm^{-1}; experimental uncertainty ±75 cm^{-1}. [b] Determined by using 9,10-diphenylanthracene in ethanol as secondary standard (ϕ 0.89); experimental uncertainty ±10%. [c] In nanoseconds; reproducibility, ±1.0 ns. [d] Best fit for a double-exponential function, 30% at 10 ns and 70% at 57 ns. [e] For solvents from pentane to ether. [f] For solvents from *n*-butyl acetate to dichloromethane.

Scheme I



moment of the exciplex, *h* is Planck's constant, *c* is the velocity of light, *a* is the radius of solvent cavity, and $f - {}^1/_2f'$ is a parameter measuring the solvent polarity from its dielectric constant and refractive index.[18] The relative polarities of these exciplexes may be determined from the least-squares analysis of the slope by plotting the values of $\bar{\nu}_{ex}$ of these compounds against $f - {}^1/_2f'$ of the solvent. When the polarity of solvent increases, the quantum yield of exciplex fluorescence, ϕ_f, decreases as the ion-pair formation becomes an effective mode of decay for the exciplexes.[19,20]

The emission maxima exhibited by **1a** and **2a** in different solvents are well within experimental errors of each other. Least-squares analyses of their $\bar{\nu}_{ex}$ vs. $f - {}^1/_2f'$ plots obtains nearly identical slopes of approximately -7.3×10^3 cm^{-1}, similar to the value reported by Weller for anthracene–diethylaniline exciplex. It is thus concluded that these exciplexes are similar in structure, and the second amino function in **1a** does not participate in the exciplex interaction. However, a line of very different slope is obtained for **1b**, $(-16.5 \pm 1.5) \times 10^3$ cm^{-1}. The results show that the exciplex from **1b** is considerably more polar than those from **1a** and **2a**, suggesting that the second amino function in **1b** does participate in the exciplex interaction. Strictly speaking, the second amino function may interact with the intermolecular binary exciplex **3** to form a ternary exciplex **4**[21] or directly with the excited anthracene chromophore to form a binary exciplex **5** (Scheme I). However, a comparison of exciplex fluorescence from **1b** with the bichromophoric **2b** does not support the latter possibility. Compound **2b** exhibits a fluorescence maximum substantially to the red of **1b** in pentane, as well as a different dependence of fluorescence maximum on the solvent polarity (table).[22] Although **1a** and **2a** exhibit a similar ϕ_f in pentane, ϕ_f of **1a** decreases sharply relative to **2a** as the solvent polarity increases in spite of the similar wavelength in their emission maxima. For the corresponding *p*-methoxy derivatives, ϕ_f of **1b** is substantially less than that of **2b** even in pentane in spite of its shorter wavelength emission.

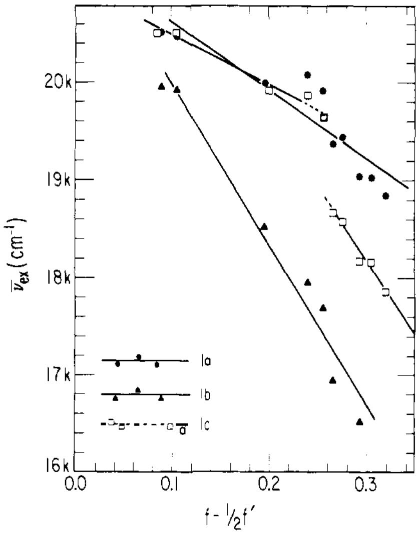


Figure 1.

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(21) In view of its high dipole moment, the ternary exciplex is assigned the unsymmetrical structure **4**; see ref 3. However, exact positions of the two amino groups in **4** remain to be determined.

(22) Compound **2b** is a good model for **5**, since an increase in chain length from 3 to 4 in naphthyl-$(CH_2)_nN(CH_3)_2$ systems did not effect the value of $\bar{\nu}_{max}$ of intramolecular exciplex; see footnote 4. We have also observed that $\bar{\nu}_{max}$ of intramolecular exciplex of **2b** in pentane is within 70 cm^{-1} of its intermolecular analogue from 9-methylanthracene–*N*,*N*-dimethylanisidine: Larson, J. R.; Horner, M. G., unpublished results.

These observations indicate that there is an additional nonradiative decay mechanism for **1** in solvents of relatively low polarity which may be the charge transfer facilitated by the termolecular interaction.[19]

Equally significant in our observations is the emission characteristics of **1c**. The solvent dependence plot on the emission maximum is a nonlinear one (Figure 1).[23] Although the position of fluorescence maximum of **1c** is indistinguishable from those of **1a** and **2a** in nonpolar solvents, they began to deviate substantially in solvents more polar than ether. If we divide the plot into portions, one including solvents from pentane to ether and the other including *n*-butyl acetate to dichloromethane, the results may be fitted into two lines of slopes of $(-5.30 \pm 0.60) \times 10^3$ and $(-15.5 \pm 1.3) \times 10^3$ cm^{-1}, respectively.[24] The data indicate that **1c** will form a binary intramolecular exciplex similar to **1a** or **2a** in nonpolar solvents, while in a more polar solvent it will form a ternary exciplex similar to that of **1b**. In spite of the difference in the IP of the dimethyl derivatives of *p*-anisidine and *p*-toluidine,[25] model compounds for the second nitrogen in **1b** and **1c**, the apparent dipole moments of exciplex derived from **1c** in solvents more polar than ether is very similar to those from **1b**. This result further substantiates the existence of intramolecular ternary exciplex **4**. Our results also imply that in a solvent of intermediate polarity such as ether both emitting species from **1c** may coexist in solution. Since exciplex emissions are broad and structureless in nature, two close-by emissions from **1c** are not resolvable from its emission spectra. In order to gain further insight into this problem, we determined the lifetimes of these exciplexes by kinetic spectroscopy, and the results are tabulated in the table. While all other exciplexes from these compounds exhibit single exponential decay, **1c** in ether exhibits a decay that is best fitted by a double-exponential function. This observation supports the existence of two emitting species from **1c** in ether.

On the basis of above observations, we conclude that (a) under proper experimental conditions, trichromophoric **1** may exist as an intramolecular ternary exciplex **4**, (b) **4** is stabilized relative to the binary exciplex **3** by increasing the polarity of the solvent, and (c) **4**, being more polar than **3**, undergoes nonradiative decay more efficiently than **3** in relatively nonpolar solvents, most likely due to ion-pair formation.

Acknowledgment. We thank the National Science Foundation, Grants No. CHE-81-12964 and CHE-80-09216, for the support of this work and Professor Graham Fleming for his advice, assistance, and encouragement.

Registry No. 1a, 82665-24-5; **1b**, 82665-25-6; **1c**, 82665-26-7; **2a**, 55789-86-1; **2b**, 55789-88-3; I, 41034-83-7; II, 22689-05-0; III, 82665-27-8; IV, 82665-28-9; V, 82665-29-0; VI, 82665-30-3; acrylic acid, 79-10-7; *N*-methylaniline, 100-61-8; *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine, 100-22-1; *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine 1,3,5-trinitrobenzene, 41912-16-7; *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine chloranil, 27237-38-3; *N*,*N*,*N'*,*N'*-tetramethyl-*m*-phenylenediamine, 22440-93-3; *N*,*N*,*N'*,*N'*-tetramethyl-*m*-phenylenediamine 1,3,5-trinitrobenzene, 82665-31-4; *N*,*N*,*N'*,*N'*-tetramethyl-*m*-phenylenediamine chloranil, 82665-35-8; *N*,*N*-dimethyl-3,4-xylidine, 770-03-6; *N*,*N*-dimethyl-3,4-xylidene 1,3,5-trinitrobenzene, 82665-32-5; *N*,*N*-dimethyl-3,4-xylidine chloranil, 82665-36-9; *N*,*N*-dimethyl-*p*-anisidine, 701-56-4; *N*,*N*-dimethyl-*p*-anisidine 1,3,5-trinitrobenzene, 82665-33-6; *N*,*N*-dimethyl-*p*-anisidine chloranil, 82665-37-0; *N*,*N*-dimethyl-*p*-toluidine, 99-97-8; *N*,*N*-dimethyl-*p*-toluidine 1,3,5-trinitrobenzene, 82665-34-7; *N*,*N*-dimethyl-*p*-toluidine chloranil, 20755-56-0; *N*,*N*-dimethylaniline, 121-69-7; *N*,*N*-dimethylaniline 1,3,5-trinitrobenzene, 16636-09-2; *N*,*N*-dimethylaniline chloranil, 82665-30-3.

Supplementary Material Available: Method of preparation, spectral data, and analytical results for compounds **1a–c** and the EDA complex method used to determine the ionization potentials of dimethylaniline, *N*,*N*-dimethyl-*p*-toluidine, and *N*,*N*-dimethyl-*p*-anisidine (6 pages). Ordering information is given on any current masthead page.

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(23) Nonlinear $\bar{\nu}_{ex}$ vs. $f - {}^1/_2 f'$ plots for **1c** were obtained in two mixed-solvent systems, hexane–dichloromethane and methylcyclohexane–tetrahydropyran, which are within experimental error of the one recorded in the figure. The corresponding plots for both **1a** and **2a** were found to be linear.

(24) If one includes only the points obtained in solvents ranging from pentane to ether for **1a** and **2a**, the slopes of $\bar{\nu}_{ex}$ vs. $f - {}^1/_2 f'$ plots of these compounds are also $\simeq -5 \times 10^3$ cm^{-1}.

(25) The IP's of *N*,*N*-dimethyl-*p*-toluidine and *N*,*N*-dimethyl-*p*-anisidine were determined by the EDA complex method using either 1,3,5-trinitrobenzene or chloranil as the acceptor. The λ_{max} of the anisidine complexes are 8 nm to the red of that of the toluidine complexes. The IP's of dimethylaniline, *N*,*N*-dimethyl-*p*-toluidine, and *N*,*N*-dimethyl-*p*-anisidine are estimated to be 7.13, 7.07, and 7.03 eV, respectively.

Measurement of Spin–Spin Distances from the Intensity of the EPR Half-Field Transition

Sandra S. Eaton

Department of Chemistry, University of Colorado at Denver
Denver, Colorado 80202

Gareth R. Eaton*

Department of Chemistry, University of Denver
Denver, Colorado 80208

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In systems containing two paramagnetic centers there is frequently considerable interest in determining the distance between the two electron spins.[1] The separation $2D$ between the low-field and high-field turning points in glass or powder EPR spectra has generally been used to obtain r, the interspin distance.[2] This analysis of the spectra is only valid under certain conditions. It assumes that the interaction between the two spins is purely dipolar or that the exchange interaction between the spins is sufficiently large that only transitions between triplet levels are observed (Figure 1, transitions 2 and 3). For intermediate values of the exchange coupling constant J, the observed separation between the turning points in the rigid spectrum is a sum of exchange and dipolar contributions. If the exchange component is ignored, the interspin distance will be underesterimated or overestimated, depending on the sign of J. Even if the magnitude of the exchange interaction permits analysis of the spectra in terms of a purely dipolar interaction, the choice of the turning points that correspond to a separation of $2D$ may be complicated by large nuclear hyperfine coupling. If the interspin vector $\vec{r}$ does not coincide with a principal axis of the hyperfine tensor for both of the electrons, then the turning points in the powder spectra will depend on the relative orientations of the hyperfine tensors and dipole tensor and on the relative magnitudes of the hyperfine and dipolar interactions. Without a computer simulation $2D$ cannot be obtained from these spectra. Also, when the EPR spectra are poorly resolved, it is difficult to estimate $2D$. Therefore it would be desirable to have another method to estimate the interspin distance.

We have done a perturbation calculation for two nonequivalent unpaired electrons. Nuclear hyperfine coupling was included for both electrons, and the angles between the nuclear hyperfine tensors and the interspin vector were allowed to take any values. The spin–spin interaction component of the Hamiltonian is given in eq 1, where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the magnetic moments for spins 1

$$\mathcal{H}_{\text{int}} = \frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1\cdot\vec{r})(\vec{\mu}_2\cdot\vec{r})}{r^5} - J\vec{S}_1\cdot\vec{S}_2 \qquad (1)$$

and 2, $\vec{r}$ is the interspin vector, and J is the isotropic exchange constant. The treatment of the nonequivalent spins is similar to that used by Pilbrow and co-workers to analyze the EPR of a B_{12}-dependent enzyme: substrate system.[3,4] It is assumed that symmetric anisotropic exchange can be neglected. Previous

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