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Nonlinear Triple Exciplexes: Thermodynamic and Kinetic Aspects of the Intramolecular Exciplex Formation between Anthracene and the Two Anchored Nitrogens of an Anthraceno-Cryptand

Frédéric Fages, Jean-Pierre Desvergne,* and Henri Bouas-Laurent

Contribution from the Laboratoire de Photochimie Organique, CNRS U.A. 348, Photophysique et Photochimie Moléculaire, Université de Bordeaux I, Talence Cedex, France.

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Abstract: The first description of an excited-state complex that is postulated to be a symmetrical nonlinear triple exciplex between anthracene and two tertiary aliphatic amines is reported. In the present molecule (AN2), which is sufficiently rigid to exclude several geometric relations between the chromophores but flexible enough to allow the interconversion of the nitrogen lone pairs, only one exciplex was observed within the time scale $\geq$100 ps (λ_{max} 490 nm in toluene and 520 nm in dichloromethane; $\Delta\bar{\nu}_{0\text{-max}}$ between exciplex maximum and locally excited state fluorescence emissions $\approx$4000–5000 cm^{-1}) with a high yield of fluorescence (ϕ_{FE} = 0.2–0.3) compared with other known triple exciplexes. Two "monomer" conformations involving the nitrogen lone pairs were detected and assigned to be "in–in" and "out–out". Despite the apparent rigidity of the molecule, the intramolecular dynamics is quite facile as the ΔG^* of interconversion "out–out" → "in–in" of both the nitrogen lone pairs is $\approx$4–5 kcal mol^{-1} at −125 °C and $\approx$6.5 kcal mol^{-1} at 20 °C (in toluene and dichloromethane). Activation energies and rate constants have been determined for the main processes of the proposed kinetic scheme.

Aromatic hydrocarbons are known to form *intermolecular* excited-state complexes[1] named "exciplexes" with tertiary amines. These fluorescent donor–acceptor complexes, where the nitrogen lone pair tends to experience the best overlap with the π aromatic cloud (Figure 1a), have a large dipole moment as demonstrated by the strong dependence of their fluorescence maxima upon solvent polarity.[1] The stabilization of the charge-transfer state, which is the main contributing state to the exciplex wave function,[1] is mainly ensured by Coulombic attraction.

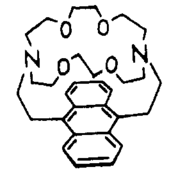
Intramolecular exciplexes can also be easily obtained by linking donor and acceptor with a variety of chains[1-3] (Figure 1b). In these systems, the chain controls the kinetics of exciplex formation and limits the possibility of mutual orientations between the nitrogen lone pair and the aromatic ring.[3,4]

"*Triple exciplexes*" involving two amines (donors) and one aromatic ring (acceptor) were first demonstrated by Knibbe and Weller[5] when using high amine concentrations to quench aromatic hydrocarbon fluorescence. In spite of a number of elegant studies devoted to that field, especially with trichromophoric systems[6] having the structure >N–(CH$_2$)$_n$–N–(CH$_2$)$_m$–Ar which allow a large degree of conformational freedom, the relative importance of the various possible modes of interaction has not been established quantitatively. Thus, with $n = m = 3$, Yang[6c,e] concluded that different folded excited-state conformations occurred, generating either a normal exciplex involving only one nitrogen (Figure 1c) or a triple exciplex incorporating both nitrogens in a linear arrangement (donor–donor–acceptor) (Figure 1d); these interactions were observed to be dependent upon the nature of solvent and chromophore. No compelling evidence for a given conformation was established.

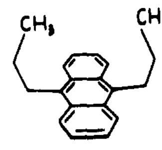
Table I. Wavelength (λ_{max}, in nm) and Molar Absorption Coefficients (ϵ, in M^{-1} cm^{-1}) of the Longest Wavelength Component of the Absorption Band of the First Electronic Transition for Compounds AN2 and R in Toluene and Methylene Chloride at 20 °C

		toluene	methylene chloride
AN2	λ_{max} (ϵ)	406 (9100)	405.5 (9100)
R	λ_{max} (ϵ)	402 (11300)	401.5 (10700)

Regarding the structure of polychromophoric interactions, the new complexing cryptand AN2 (see formulae), previously designed[7] to get cation-modulated fluorescence, presents a quasirigid molecular framework in which the three different chromophores (two donors and one acceptor) are symmetrically held together in well-defined mutual orientations (Figure 1e and formulae). Therefore this unusual trichromophoric system is expected to provide new insight into the exciplex photophysics.



AN2



R

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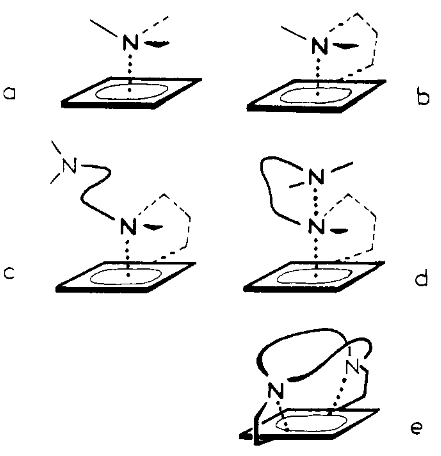

Figure 1.

This paper describes spectroscopic properties of AN2 (electronic absorption, fluorescence emission, and ^{1}H NMR spectra) and reports quantitative data supporting the postulation of the first symmetrical nonlinear triple exciplex.

Experimental Section

The synthesis and purification of AN2 and the reference compound R were described in a previous paper.[7] The UV spectra were recorded on a Varian Cary 219 and fluorescence spectra on a Perkin-Elmer MPF 44 apparatus. In all the experiments, the solutions (concentration $<10^{-5}$ M) were degassed by the freeze–pump–thaw technique. The temperature of the cell, monitored by a platinum temperature sensor (±0.5 °C), was regulated by nitrogen flow. The fluorescence quantum yields were determined as previously published.[8a] Decay measurements were performed by using the single-photon counting technique (Applied Photophysics); the decay parameters were determined by a nonlinear least-squares deconvolution method[8b] and the success of the fits was evaluated by the reduced χ^2 (range from 0.95 to 1.2), the randomly distributed weighted residuals about zero, and the autocorrelation function of weighted residuals.[8c] Toluene (Aldrich, Gold Label) was refluxed over sodium and distilled just prior to use, and methylene chloride was refluxed and distilled over P_2O_5.

The ^{1}H NMR spectra were run on a Bruker AC 200 (200 MHz). Normal and decoupled spectra were used in the analysis of the NMR data. All data were checked by a computer simulation of the NMR spectra. Toluene-d_8 (Commissariat ã l'Energie Atomique (CEA), 99.93%) and methylene-d_2 chloride (CEA, 99.3%) were used as solvents. The samples were purged with nitrogen and the tubes were sealed off.

Results and Discussion

Electronic Absorption Spectra. The UV absorption spectra of compounds AN2 and R (9,10-di-*n*-propylanthracene) show the same trends, in the two solvents studied, for the first electronic transition band ($^1L_a \leftarrow A$) (the 1,10-diazacrown ether chromophore absorbs light at $\lambda < 300$ nm). However, at room temperature, some noticeable hypo- and bathochromic effects are observed for AN2 (see Table I); they were assigned[7] to an intramolecular ground-state interaction between the nitrogen lone pairs and the aromatic π cloud.

No significant modifications are detected for R when the spectra are recorded versus temperature except the usual sharpening of the vibronic structure when the temperature is decreased. In contrast, AN2 displays a band splitting at low temperatures ($T \approx 180$ K) (see Figure 2) indicating the likely occurrence of two different absorbing species. This split band spectrum smoothly coalesces when the temperature is increased, leading to a broader single banded spectrum at $T > 270$ K. By analogy with the spectrum of R, the "high-energy" absorption spectrum (for instance the band with $\lambda_{max} = 401$ nm, 180 K) suggests a conformer where the nitrogen lone pairs and aromatic ring do not interact.

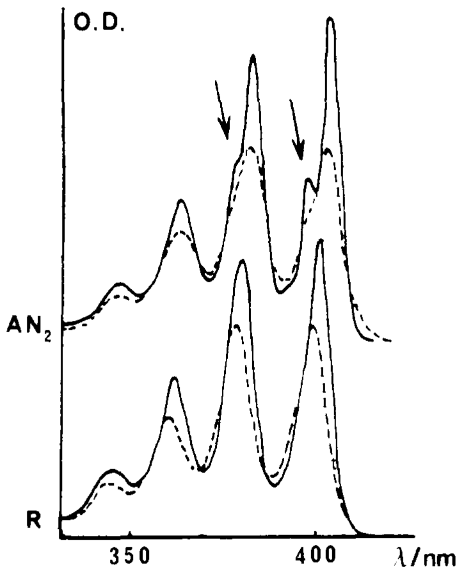

Figure 2. UV absorption spectra in toluene of compounds AN2 (top) and R (bottom) at −80 °C (—) and +25 °C (---). Note the shoulders (arrows) at low temperature for AN2.

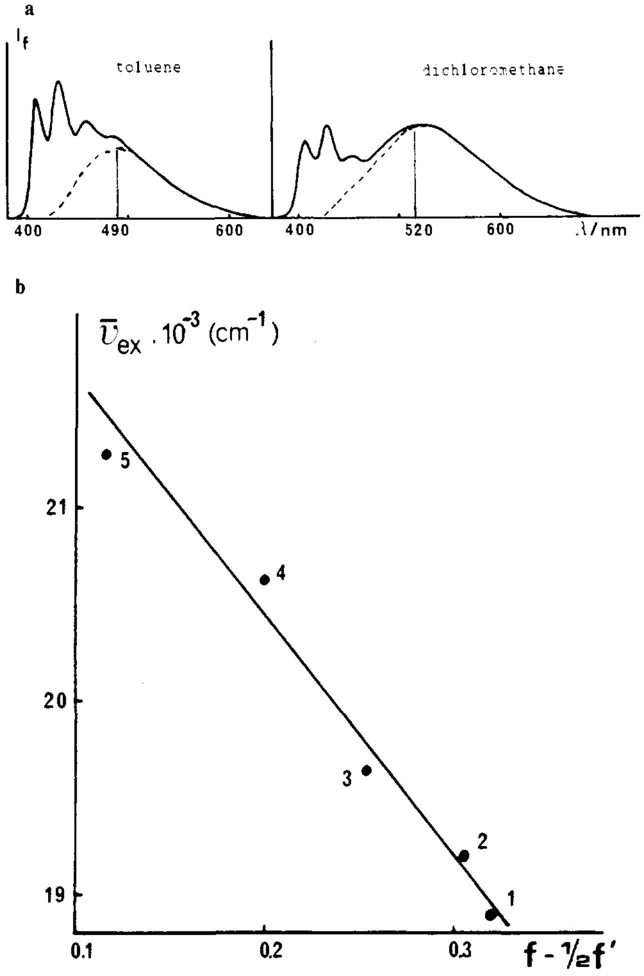

Figure 3. (a) Corrected fluorescence emission of AN2 in degassed toluene and dichloromethane ($c \leq 10^{-5}$ M) at 20 °C. The exciplex contribution (---) is obtained from difference spectra between AN2 and R. (b) Wavenumber of the exciplex emission maximum, at 20 °C, of AN2 as a function of solvent polarity parameter $f - \frac{1}{2}f'$; $f = (\epsilon - 1)/(2\epsilon + 1)$, $f' = (n^2 - 1)/(2n^2 + 1)$. Solvents ($f - \frac{1}{2}f'$): (**1**) dichloromethane (0.319), (**2**) tetrahydrofuran (0.306), (**3**) diethyl ether (0.256), (**4**) trichloroethylene (0.197), (**5**) methylcyclohexane (0.106).

Fluorescence under Stationary Conditions. a. At Room Temperature. The fluorescence spectra of compound AN2 in a variety of solvents (see Table II) show the usual anthracenic emission from the locally excited state and a red-shifted, structureless

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Table II. Fluorescence Emission Quantum Yield of Degassed Solutions of AN2 in Different Nonprotic Solvents at 20 °C[a]

solvent	ϕ_{FT}	ϕ_{FM}	ϕ_{FE}	ϕ_{FE}/ϕ_{FM}
methylcyclohexane[b]	0.38	0.25	0.13	0.53
diethyl ether[b]	0.21	0.14	0.07	0.50
benzene	0.64	0.32	0.32	1.00
toluene	0.66	0.30	0.36	1.20
trichloroethylene	0.56	0.29	0.27	0.92
tetrahydrofuran	0.29	0.06	0.23	3.76
dichloromethane	0.40	0.13	0.27	2.07
acetonitrile	0.20	<0.01	0.19	>19

[a] ϕ_{FT} = total fluorescence quantum yield, ϕ_{FM} = "monomer" (locally excited state) fluorescence quantum yield, ϕ_{FE} = exciplex fluorescence quantum yield. [b] Nondegassed.

emission attributed[7] to an intramolecular exciplex between anthracene and the nitrogen lone pairs (see Figure 3). The shape of the exciplex emission spectra can be obtained from difference spectra between AN2 and R after normalization at the 0–0 transition. If the position of the maximum varies slightly with temperature (<10 nm between 350 and 180 K) it is rather sensitive to the polarity of the solvent, showing the charge-transfer character of the emitting complex. In solvents of low polarity, this effect can be analyzed quantitatively according to the Weller equation.[5a,9]

$$\bar{\nu}_{ex} = \bar{\nu}_{ex}(0) - (2\mu_{ex}^2/hc\rho^3)(f - {}^1\!/\!_2 f')$$

On the basis of a plot of $\bar{\nu}_{ex}$(max) as a function of $(f - {}^1/_2 f')$ which shows, within experimental errors, no deviation from linearity, we calculate a slope of −11 750 cm^{-1} which is in the range of values published by Yang[6e] for polychromophoric molecules containing one anthracene and two nitrogens. From the X-ray analysis[10] of AN2, the distance between the nitrogen atoms and the anthracene ring is known to be 3.6 Å (it is comparable with the usual separations between exciplex-forming components[11]). Accepting this value as the average distance also in solution and taking into account the fact that the nitrogens are ensconced inside the cavity (the solvent sphere has a diameter[11] ρ approximated to ca. 5.5 Å, higher than the nitrogen anthracene distance), the excited-state dipolar moment μ_{ex} could be estimated to be at least equal to 14 D. This value is not far from that found by Nakajima[1d] for the intermolecular exciplex between anthracene and tri-*n*-butylamine (12.8 D, $\rho \approx 5.5$ Å). These evaluations rest on several approximations and should be considered as tentative. Moreover, the dipole moments depend on the charge and on the distance between the nitrogen and the aromatic hydrocarbon. A similarity between experimental dipole moments does not necessarily imply similar exciplexes. In our case, contrary to Nakajima's, the two components of the triple exciplex should form an angle between the axes of the nitrogen lone pair and of the π electrons, respectively. Thus the dipole moment value is indicative of a charge-transfer character and cannot invalidate the proposal of a triple exciplex.

The fluorescence emission quantum yields (Table II) are relatively high in comparison with data for quasilinear excited complexes ($A^* \cdots N_1 \cdots N_2$) involving two nitrogens and one anthracenic ring in which the second nitrogen acts as an extra fluorescence quencher;[6e,12] such a linear geometry is sterically forbidden in the present case. The high fluorescence yield of the AN2 exciplex, in contrast with the other triple exciplexes, is probably due to the fact that this exciplex looks like "normal" exciplexes in which there is an interaction between a single nitrogen and an aromatic hydrocarbon. In triple linear exciplexes, an important contribution to the quenching originates[13e,f] in the formation of a three-electron bond between two nitrogens, for a N···N distance[13] of 2.1–2.3 Å; this arrangement can be attained in a flexible system but seems very unlikely in the present case where the distance between the two nitrogen centers (5.2 Å) is too high.[10,13g]

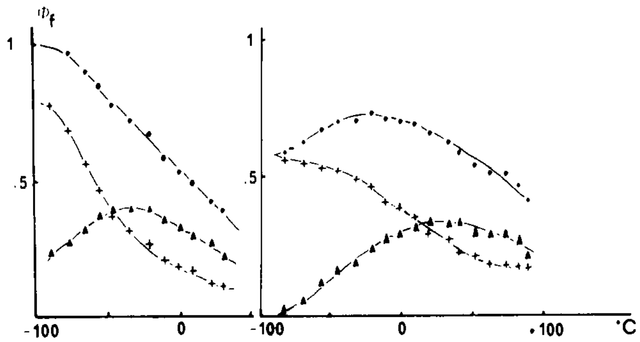

Figure 4. Total (●●●), locally excited state ϕ_{FM} (++), and exciplex ϕ_{FE} (▲▲) fluorescence quantum yields of AN2 versus temperature in dichloromethane (left) and toluene (right).

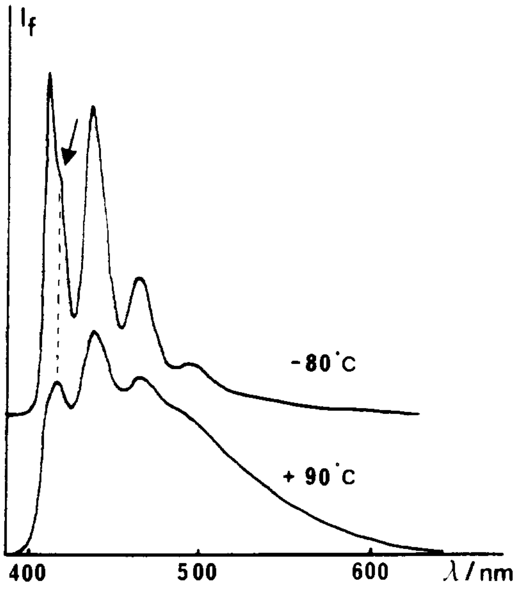

Figure 5. Corrected fluorescence emission spectra of AN2 in degassed toluene ($c \leq 10^{-5}$ M) at −80 and +90 °C. The arrow denotes at −80 °C the low energy monomer contribution (see text). The excitation spectra recorded at −80 °C (λ_{obs} = 405 nm) display two separated monomer contributions.

b. Influence of Temperature. The fluorescence quantum yields (locally excited state "monomer" fluorescence ϕ_{FM} and exciplex fluorescence ϕ_{FE}) have been plotted for AN2 versus temperature in toluene and dichloromethane (Figure 4), which remain liquid in a wide range of temperature; these two solvents (as will be presented later) have been selected for an NMR study.

In toluene, no exciplex emission was detected below a threshold temperature (183 K). As the temperature was raised, the exciplex fluorescence intensity increased to reach a solvent-dependent maximum (toluene, 300 K; dichloromethane, 230 K). Above this

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(9) $\bar{\nu}_{ex}$ is the fluorescence maximum of the exciplex in a given solvent (in cm^{-1}), $\bar{\nu}_{ex}(0)$ is the maximum in vacuum, μ_{ex} is the dipole moment of the exciplex, *h* is Planck's constant, *c* is the velocity of light, ρ is the radius of solvent cavity, and $(f - {}^1/_2 f')$ is a parameter measuring the solvent polarity from its dielectric constant and refractive index: $f = (\epsilon^2 - 1)/(2\epsilon + 1)$ and $f' = (n^2 - 1)/(2n^2 + 1)$.

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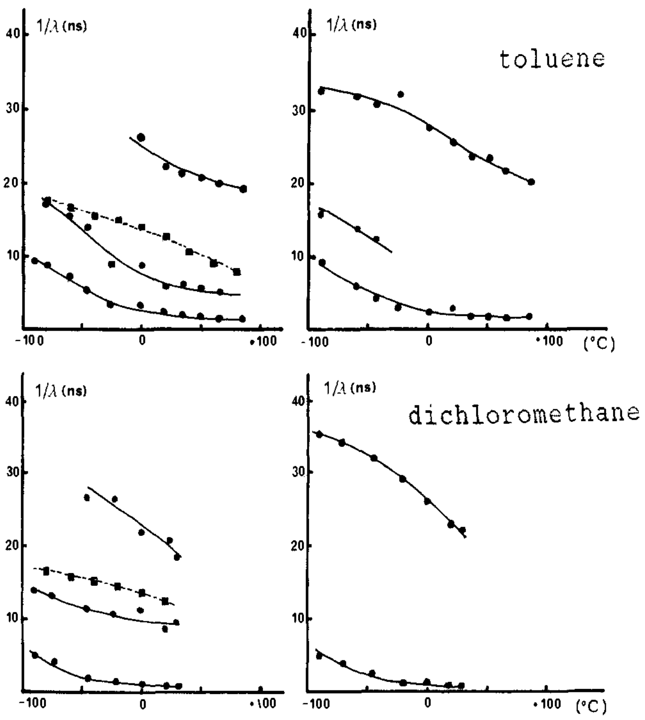
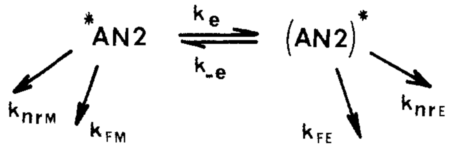


Figure 6. Fluorescence decay lifetimes ($1/\lambda_i$) of AN2 in toluene (top) and dichloromethane (bottom). Left: "monomer" region (410 nm). Right: exciplex region (>530 nm). The fluorescence decay lifetime of R is represented by dashed lines.

Scheme I[a]



[a] k_{FM}, k_{FE}: fluorescence rate constants of "locally excited state" and exciplex emissions. k_e, k_{-e}: exciplex formation and dissociation rate constants. $k_E = k_{FE} + k_{nrE}$: reciprocal lifetime of exciplex.

point, the exciplex emission intensity decreased slightly with increasing temperature.

It is of interest to pay attention to the temperature dependence of the "monomer" fluorescence emission as exemplified with toluene in Figure 5. At "high" temperature (363 K) the vibronic bands are broad with the first band peaking at 414 nm, whereas at "low" temperature (193 K), a second "monomer" type emission appears at 409 nm, and increases with cooling of the solution due to the sharpening of the bands.

The excitation spectra recorded on the "monomer" and exciplex parts reveal two distinct energetically close contributions (which look like the low-temperature absorption spectrum) connected with a clear balancing of their respective weights (by scanning the "monomer" and the exciplex regions) in accordance with the presence of two locally excited conformers.

Fluorescence under Dynamic Conditions. The fluorescence emission decay of AN2 monitored at 410 nm on the "monomer" region was fitted with a sum of three exponentials above a critical temperature (−50 °C for dichloromethane and 0 °C for toluene) and a sum of two exponentials below this temperature (see Figure 6).

In the exciplex region (λ > 530 nm) the emission decay is fitted with a three-exponential function below 0 °C for toluene (with a negative preexponential term) and a difference of two exponentials above that temperature. In dichloromethane, the exciplex emission fluorescence decay can be analyzed as a difference of two exponentials for the whole explored temperature range (−90, +40 °C).

The decay measurements recorded on AN2 are not compatible with the classical kinetic Birks' scheme[14] where one monomer species is in interconversion with one exciplex (see Scheme I). In that case, the fluorescence decays are fitted with a sum of two exponentials for the monomer region and a difference of two exponentials for the exciplex wavelength range. The rate parameters λ_1, λ_2 have to be identical for the monomer and exciplex regions with a ratio of the preexponential terms equal to −1 for the exciplex decay function.

In the present case, the fluorescence decay behavior is compatible with the simultaneous presence of two distinct sets of monomers (in accordance with electronic absorption and fluorescence emission data) and one exciplex. That only one

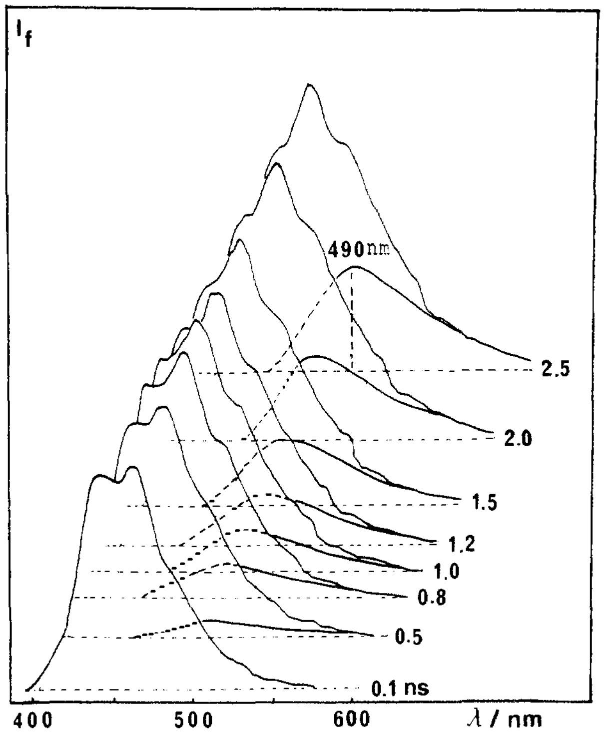
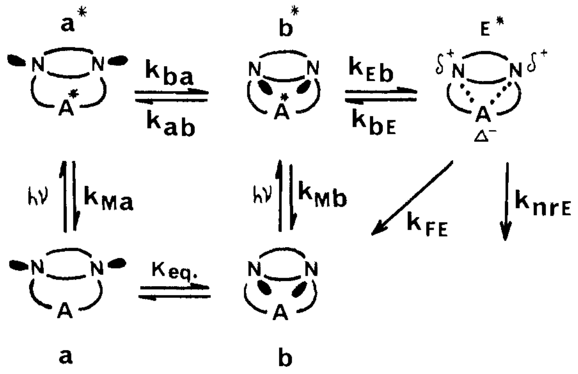


Figure 7. Time-resolved fluorescence[21] spectra (0.1 to 2.5 ns after the exciting pulse, 353 nm) of AN2 in toluene at 20 °C. No fluorescence due to exciplex is detectable up to 100 ps after the exciting pulse. The spectra are normalized at the first vibronic band and the exciplex contribution is obtained from difference spectra between the emission recorded 0.1 ns after excitation (reference) and the other emissions up to 2.5 ns.

Scheme II[a]



[a] k_{Ma}, k_{Mb}: reciprocal lifetimes of conformers a* and b*. k_{ba}, k_{ab}: interconversion rate constants between conformers a* and b*. k_{Eb}, k_{bE}: exciplex formation and dissociation rate constants. $k_E = k_{FE} + k_{nrE}$: reciprocal lifetime of exciplex. At 293 K in toluene: $k_{ba} = 1.2 \times 10^8$ s^{-1}; $k_{ab} = 2.3 \times 10^7$ s^{-1}; $k_{Eb} = 3.3 \times 10^8$ s^{-1}; $\tau_E = 1/(k_{FE} + k_{nrE}) = 28$ ns; $k_{FE} = 1.2 \times 10^7$ s^{-1}; k_{nrE} (nonradiative decay from exciplex) = 2.2 × 10^7 s^{-1}; $K_{eq} \approx 6$.

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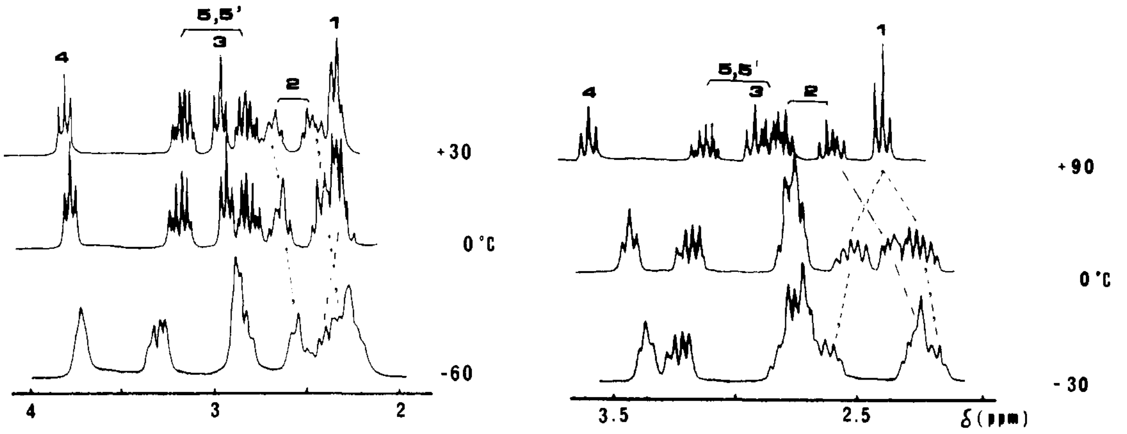

Figure 8. Variation of the aliphatic proton resonance signals of AN2 with temperature (200 MHz, chemical shifts relative to Me_4Si) in dichloromethane-d_2 (left) and toluene-d_8 (right). The numbers refer to different protons of the "N_2O_4" ring, as defined in the structural formula (see Figure 9).

exciplex is involved in the photophysics of AN2 is supported by time-resolved fluorescence spectra in the picosecond range; indeed the buildup of the excited complex emission peaking at 490 nm (detected in toluene between 50 ps and 2.5 ns (Figure 7)) corresponds to the short lifetime component in the monomer decay. In Scheme II, "a" and "b" will represent two ground-state conformers (as suggested from UV and fluorescence excitation spectra), a* and b* the corresponding excited monomer species, and E* the intramolecular exciplex.

From the excitation spectra recorded at $\lambda > 530$ nm and the fluorescence decays, E* is assumed to be formed via "b*" geometrically close to the red-shifted absorbing species monomer "b" ($\lambda_{max} = 406$ nm in toluene). The other species "a*" formed (in part by direct excitation of "a" in the ground state) could not directly generate the exciplex E*, but forms b* during its lifetime.

Although "a" and "b" were detected by UV absorption and fluorescence spectroscopy, their relative amount was impossible to determine owing to the overlapping of the spectra. As it has been shown that inversion of nitrogen occurs on the ^1H NMR time scale for other cryptands,[15] an ^1H NMR spectroscopy study was carried out in order to solve this problem.

Study of the ^1H NMR Spectrum of AN2. The ^1H NMR spectrum of AN2 is sensitive to temperature, especially the signals due[16] to the protons in the vicinity of the nitrogen atoms (sites 1, 2, 3, and 4, see Figure 8).

These local spectral modifications are believed to be mainly due to molecular framework relaxation associated with the conformational interconversion of the nitrogens as observed in other systems.[15] The protons belonging to sites 1,2 and 3,4 (and also 5 and 5′) were analyzed as ABCD patterns as depicted in Figure 9. The coupling constants were found to be weakly sensitive to temperature in contrast to the chemical shifts (see Figure 10).

Assuming a fast exchange regime on the NMR time scale (lifetime < 10^{-6} s), the observed spectrum may be considered as due to a single species whose NMR parameters (chemical shifts ν_{av}) are the relevant averages of those of the individual species (ν_i) which should be suitably weighted to take account of different populations X_i.

$$\nu_{av} = \sum_i X_i \nu_i \qquad (1)$$

As indicated in the preceding paragraph, it appears reasonable to consider for AN2 two main sets of conformers "a" and "b" in the ground state which are in equilibrium: a $\rightleftharpoons$ b, with $K = [b]/[a] = \exp(-\Delta H/RT + \Delta S/R)$. Then eq 1 can be formulated as follows

$$\nu_{av} = X_a \nu_a + X_b \nu_b \qquad (2)$$

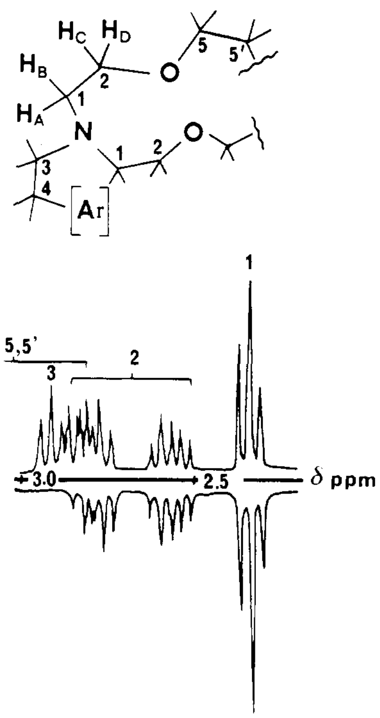

Figure 9. Top: 200-MHz ^1H NMR spectrum between 2.0 and 3.0 ppm of AN2 in toluene at 90 °C. Bottom: computer-simulated spectrum for protons 1 and 2.

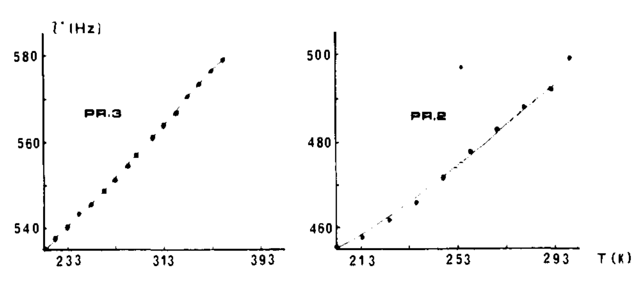

Figure 10. (●●●) Temperature dependence of the chemical shifts of protons 2 (PR2, dichloromethane) and 3 (PR3, toluene). (—) Fits of these data with eq 3. The coupling constants (in Hz) $J_{1,2}$ (−12.5), $J_{1,3}$ (6.3), $J_{1,4}$ (5.9), $J_{2,3}$ (5.9), $J_{2,4}$ (6.1), and $J_{3,4}$ (−10.2) were not found to be very sensitive to solvent and temperature.

The population of the two conformers "a" and "b" may be expressed as a function of the energy difference[17] between the conformers, and eq 3 can be derived (with $X_a + X_b = 1$).

$$\nu_{av} = (\nu_a - \nu_b)\{1/[1 + \exp(-\Delta H/RT + \Delta S/R)]\} + \nu_b \qquad (3)$$

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[15] (a) Graf, E.; Kintzinger, J. P.; Lehn, J. M.; LeMoigne, J. *J. Am. Chem. Soc.* **1982**, *104*, 1672. (b) Dietrich, B.; Lehn, J. M.; Sauvage, J. P.; Blanzat, J. *Tetrahedron* **1973**, *29*, 1629.

[16] Detailed information concerning the attribution of signals was given in ref 7b.

[17] See for instance: Leeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

Table III. Kinetic Parameters Respectively for Conversion of Conformer "a" to Conformer "b" in the Singlet Excited State, Exciplex Formation from "b*", and Decay of Exciplex of AN2 in Toluene and Dichloromethane

process	k^0, s^{-1}	E_a, kcal/mol	k(20 °C),[a] s^{-1}	solvent
k_{ba}	4.9×10^{10}	3.6	1.1×10^{8}	toluene
a* → b*	4.8×10^{8}	1.4	4.4×10^{7}	dichloromethane
k_{Eb}	1.4×10^{10}	2.2	3.3×10^{8}	toluene
b* → E	4.8×10^{10}	2.2	1.1×10^{9}	dichloromethane
decay of exciplex	4.6×10^{7}	0.16	3.5×10^{7}	toluene
k_E	5.1×10^{7}	0.23	3.4×10^{7}	dichloromethane

[a] $k = k^0 \exp(-E_a/RT)$.

Using eq 3 to fit experimental data for sites 1, 2, 3, and 4 leads to ΔS and ΔH values if the proposed equilibrium is valid.

Experimental data and simulated curves are given in Figure 10 for 1 proton for sites 2 and 3. For all of the 4 sites analyzed (8 protons) similar values of ΔS ($\approx 0 \pm 0.2$ ue) and ΔH (-1.0 ± 0.2 kcal/mol) are obtained in both solvents, which strongly supports the above assumption that a single conformational rearrangement occurs (a $\rightleftarrows$ b).

Interpretation of Fluorescence Measurements within the Framework of Kinetic Scheme II. In the low-temperature region (where the exciplex component is not observed on the monomer decay) when it is assumed that $k_{bE} \ll k_E$ and $k_{ab} \ll k_{Eb} + k_M$ (k_{MA} and k_{MB} being supposed for simplification not very different and similar to k_M), the time dependence of the emission of the "monomer" excited state and exciplex state are given, as demonstrated elsewhere,[18] by eq 4 and 5.

$$I_M(t) \approx X_a\left(1 + \frac{k_{ba}}{k_{Eb} - k_{ba}}\right) \exp[-(k_{ba} + k_M)t] + \left(X_b - \frac{X_a k_{ba}}{k_{Eb} - k_{ba}}\right) \exp[-(k_{Eb} + k_M)t] \quad (4)$$

$$I_E(t) \approx \left(\frac{X_a k_{ba}}{k_M + k_{ba} - k_E} + \frac{X_b k_{Eb} - k_{ba}}{k_{Eb} + k_M - k_E}\right) \exp[(-k_E)t] + \left(\frac{X_b k_{Eb} - k_{ba}}{k_E - k_M - k_{Eb}}\right) \exp[-(k_{Eb} + k_M)t] + \left(\frac{X_a k_{ba}}{k_E - k_M - k_{ba}}\right) \exp[-(k_{ba} + k_M)t] \quad (5)$$

The kinetic analysis of the fluorescence decays (see Figure 6) shows that the exciplex is formed via the shortest lifetime component that can be related to "b*". The biexponential decay of the exciplex part (above a critical temperature >0 °C for toluene) might be due to the negligible contribution of conformer "a" for the exciplex formation or to the fact that the decay times of the two components come very close.

With use of eq 4 and 5, k_{ba}, k_{Eb}, and k_E can be readily calculated in the low-temperature region (Table III) (k_M being taken equal to that of R in toluene or dichloromethane at the same temperature). Plotting ln k versus $1/T$ yields a linear relation for k_{Eb}, k_{ba}, and k_E (Figure 11) from which the preexponential factors k°_{Eb}, k°_{ba}, and k°_E and the respective activation energy E_a can be derived (Table III).

These values are in the range of those given by De Schryver for intramolecular exciplex formation in ω-phenyl-α-(*N*,*N*-dimethylamino)butane, where only one nitrogen is involved.[18]

Assuming[19] a similar energy difference (and also the same activation barriers) between a* and b* as between "a" and "b" in the ground state (at this wavelength, the excited state energy being localized in the aromatic ring whose geometric modifications are supposed to not affect significantly the "N_2O_4" ring molecular dynamics), it is then possible to estimate k_{ab} (from [b]/[a] determined by NMR measurements). At 20 °C with [b]/[a] ≈ 6, k_{ab} is found to be equal to 1.8×10^7 s^{-1} in toluene and 7.3×10^6 s^{-1} in methylene chloride.

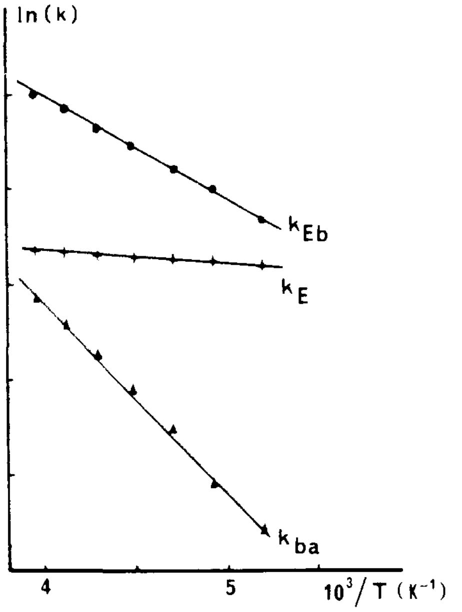

Figure 11. Plots for AN2 in toluene of the natural logarithm of the rate constants k_{Eb}, k_E, and k_{ba} versus the reciprocal absolute temperature.

Table IV. Activation Parameters for the Nitrogen Lone Pairs Inversion of AN2 (a* → b*) and Kryptofix [222][a]

	solvent	T, K	ΔS^*, cal mol^{-1} T^{-1}	ΔH^*, kcal mol^{-1}	ΔG^*, kcal mol^{-1}
AN2	toluene	293	−11.7	3.0	6.4
		148	−10.3	3.3	4.8
	dichloromethane	293	−20.9	0.8	6.9
		148	−19.5	1.1	4.0
Kryptofix [222]	dichloromethane	148			6.5

[a] ΔH^* and ΔS^* were obtained from E_a and k^0 of Table III, using the relations $\Delta H^* = E_a - RT$ and $\Delta S^* = R$ [ln A − ln (RT/Nh) − 1].

Despite the scarcity of quantitative data on the inversion of the nitrogen lone pairs of AN2 and related compounds (Table IV), a few comments will be made: (i) The energy barrier ($\Delta G^* \approx 4$ kcal mol^{-1} at −125 °C) we have determined in CH_2Cl_2 is distinctly lower than the value observed by Lehn[15] for the Kryptofix [222] ($\Delta G^* \approx 6.5$ kcal mol^{-1} at −125 °C in CF_2HCl); a likely explanation could lie in the strain introduced by the rigid aromatic ring into the cryptand, which would increase the initial state free energy relative to that of Kryptofix [222] and would not affect the activated complex to such an extent. (ii) Moreover, the determination of activation parameters in toluene and dichloromethane allows a deeper insight into the inversion process; the difference in ΔH^* and ΔS^* points to the participation of solvent molecules in the formation of the activated complex, in agreement with a negative ΔS^* and the fact that it is much more negative for CH_2Cl_2, the solvent for which ΔH^* is much smaller, suggesting some sort of link[20] with AN2 in the transition state. It is interesting to note that the advantage given by CH_2Cl_2 in terms of

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[18] Van der Auweraer, M.; Gilbert, A.; De Schryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4007.

[19] Because of the rather large errors in the determination of the preexponential terms of the decay necessary to calculate a^*/b^*, this ratio was estimated from ground-state population.

[20] That CH_2Cl_2 may interact with the diazacrown part of AN2 is in agreement with a recent paper of Tabushi dealing with the complexation of this compound inside a tetraazaparacyclophane. The inclusion of methylene chloride controlled the conformational properties of the molecule and its crystallization packing mode. Tabushi, I.; Yamamura, K.; Nonoguchi, H.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1984**, *102*, 2621.

[21] For experimental details see: Gilabert, E.; Lapouyade, R.; Rullière, C. *Chem. Phys. Lett.* **1988**, *145*, 262.

J. Am. Chem. Soc. 1989, 111, 102-107

activation enthalpy is cancelled by an important relative loss of entropy (10 eu) compared with toluene, with the result that the two solvents have a similar efficiency.

Arguments in Favor of a Symmetrical Triple Exciplex. 1. From the above spectroscopic studies it appears that only two main sets of conformers participate in the photophysics of AN2. Of note is the strong tendency of the molecule to adopt the highest symmetric geometry throughout a wide temperature range (−80 + 90 °C) in the ground state as demonstrated by NMR (C_{2v} symmetry). This is why the two sets have been denoted "in–in" and "out–out" and why the "in–out" geometry has been discarded.

2. A symmetrical exciplex can be built up from the "in–in" b* conformer with the minimum of atomic movement and a weak activation energy (2.2 kcal/mol); thus, the lone pairs of the two nitrogen atoms can simultaneously experience the best overlap with the π electron cloud at the meso positions, i.e., those of the highest electronic density. Inspection of molecular models suggests that an "in–out" conformation for AN2 conducive to a mononitrogen exciplex would be strained.

3. Single crystals of AN2 (grown in toluene solutions) emit only the exciplex fluorescence[7c,10] with a decay of 18 ns at 20 °C, which is of the same order of magnitude as one of the components of the exciplex emission in toluene and dichloromethane; the spectrum is similar in shape and in maximum wavelength (λ_{max} ≈ 520 nm) to those obtained from toluene (490 nm) and dichloromethane (520 nm). Moreover, owing to the large distance between the parallel anthracenic rings (≈10–11 Å) in the crystal, intermolecular excimer formation can be ruled out. In the solid state, the two nitrogen lone pairs are symmetrically oriented *inside* the cavity ("in–in").[10] That the conformation "b" which, in fluid solution, leads to the exciplex and which is dominant at low temperature ([b]/[a] ≈ 15 at −90 °C) has the same geometry as that found in crystals is beyond doubt. In contrast, the "a" species, which absorbs light like the reference compound (R), should exhibit "out–out" orientation of its nitrogen lone pairs presumably orthogonal to the π aromatic electrons, in agreement with the absence of interaction between the chromophores. This conclusion is reinforced by inspection of molecular models which indicate that "b" and "a" conformers, although both strained, could be in interconversion.

Conclusion

We have described an excited-state complex between two aliphatic amines and one aromatic hydrocarbon, which is postulated to be the first symmetrical nonlinear triple exciplex.

This new exciplex has a relatively high fluorescence quantum yield compared to other triple exciplexes. A detailed kinetic and thermodynamic analysis allowed a description of the molecular dynamics of the system.

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Supplementary Material Available: Tables of decay parameters of AN2 as a function of temperature (2 pages). Ordering information is given on any current masthead page.

EXAFS Studies on Pig Plasma Amine Oxidase. A Detailed Structural Analysis Using the Curved Wave Multiple Scattering Approach

P. F. Knowles,[*,†] R. W. Strange,[‡] N. J. Blackburn,[‡] and S. S. Hasnain[*,§]

Contribution from the Astbury Department of Biophysics, University of Leeds, Leeds LS2 9JT, UK, Synchrotron Radiation Source, SERC Daresbury Laboratory, Warrington WA4 4AD, UK, and the Department of Chemistry, University of Manchester Institute of Science and Technology, P.O. Box 88, Manchester M60 1QD, UK. *Received September 21, 1987*

Abstract: EXAFS studies have been carried out on pig plasma amine oxidase containing one copper and two copper atoms. The data for the two forms are essentially identical and are consistent with the presence of four low-Z scatterers and one heavier scatterer in the primary ligand shell. There is evidence that the heavy scatterer is a sulfur atom coordinated at 2.38 Å. The four low-Z scatterers distribute themselves about the copper atom at two discrete distances, 2.00 and 1.90 Å. The 2.00-Å distance is accounted for by two nitrogens and the outer shell analysis is consistent with this as imidazole coordination. The two low-Z scatterers at 1.90 Å are consistent with Cu–O coordination, probably arising from phenolate and/or OH^-. The analysis provides no direct evidence for or against the presence of PQQ coordinated to copper.

Amine oxidases catalyze the oxidative deamination of amines to the corresponding aldehyde, hydrogen peroxide and ammonia. There are two categories of amine oxidase: those containing copper (E.C.1.4.3.6) and those containing flavin (E.C.1.4.3.4). Both categories of amine oxidase have important roles in the catabolism of biogenic amines, including histamine, serotonin, and catecholamines, while the copper-containing enzymes are also involved in cross-linking reactions in connective tissue.[1]

The copper-containing amine oxidase from pig plasma (PPAO) is one of the better characterized in this class of enzyme. The homogeneously pure enzyme has a molecular weight of 190 000 composed of two subunits with equal molecular weight.[2,3] It is known that the enzyme contains a novel cofactor pyrrolo quinoline quinone (PQQ) in addition to copper.[4] The structure and function

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[†] Univeristy of Leeds.

[‡] University of Manchester Institute of Science and Technology (UMIST).

[§] SERC Daresbury Laboratory.

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