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## Exciplex Substitution ($S_{ex}$). A New Photophysical Process

*Sir:*

The role of singlet exciplexes in 2 + 2 photocycloadditions to the phenanthrene chromophore has been conclusively proven[1] by an exciplex quenching method. We have established the charge-transfer nature of the quenching mechanism[1b,2] but the fate of the three components of the interaction remains unknown. We now report that one mode of interaction of an exciplex with a quencher is an exchange of partners, which we term exciplex substitution, $S_{ex}$, recognizing the formal analogy to ground state nucleophilic ($S_N$) and electrophilic ($S_E$) substitutions.

$$M^* + Q_1 \rightleftharpoons (MQ_1)^* \qquad (1)$$

$$(MQ_1)^* + Q_2 \rightarrow (MQ_2)^* + Q_1 \quad S_{ex} \qquad (2)$$

Quenching of the 3,10-dicyanophenanthrene (3,10-$(CN)_2P$)-*trans*-anethole (*t*-An) exciplex[3] ($MQ_1^*$, $\lambda_{max}$ = 466 nm, $\tau$ = 37.5 ns) by diethylaniline ($PhNEt_2$) is accompanied by the formation of a new species with emission properties very similar to those of the 3,10-$(CN)_2P$-$PhNEt_2$ exciplex ($MQ_2^*$, $\lambda_{max}$ 535 nm, $\tau$ = 100 ns), and the observation of an isoemissive point at 519 nm (Figure 1). The intensity of the new emission is always much greater than predicted from the Stern-Volmer slopes for competitive quenching of M* by *t*-An (265 M$^{-1}$) and $PhNEt_2$ (420 M$^{-1}$) and the concentrations of *t*-An and $PhNEt_2$. Thus at [*t*-An] = $8.1 \times 10^{-2}$ M and [$PhNEt_2$] = $4.6 \times 10^{-3}$ M (Figure 1, B) 58% of the $MQ_1$ emission (Figure 1, A) is quenched and the $MQ_2^*$ emission is 57% as intense as when [$PhNEt_2$] = $5 \times 10^{-2}$ M (Figure 1, D) in the absence of *t*-An. The fraction of M* quenched by $PhNEt_2$ directly in this experiment is not 57% but only 9%. If the [*t*-An] is increased to 0.225 M but the [$PhNEt_2$] is maintained at $5 \times 10^{-3}$ M, small *increases* in the emission intensities of *both* exciplexes are observed (Figure 1, E) together with a marked decrease in monomer emission intensity. Steady-state analysis leads to the prediction that the ratio of $MQ_2$ to monomer emission intensity should be independent of [*t*-An] if quenching of M* by $PhNEt_2$ is the only route to $MQ_2$. Our observations show that *quenching of one exciplex can lead to the formation of another exciplex.*

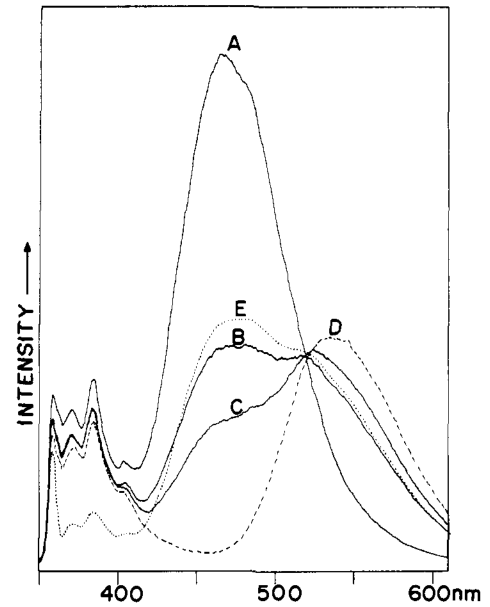

**Figure 1.** Uncorrected emission spectra in outgassed benzene, [3,10-$(CN)_2P$] = $1.1 \times 10^{-3}$ M: (A) [*t*-An] = $8.1 \times 10^{-2}$ M; (B) [*t*-An] = $8.1 \times 10^{-2}$ M, [$PhNEt_2$] = $4.6 \times 10^{-3}$ M; (C) [*t*-An] = $8.1 \times 10^{-2}$ M, [$PhNEt_2$] = $10^{-2}$ M; (D) [$PhNEt_2$] = $5 \times 10^{-2}$ M; (E) [*t*-An] = $2.25 \times 10^{-1}$ M, [$PhNEt_2$] = $4.6 \times 10^{-3}$ M.

More direct evidence for $S_{ex}$ has been obtained by nanosecond flash emission spectroscopy.[4] Excitation of 3,9-dicyanophenanthrene,[5] 3,9-$(CN)_2P$ ($10^{-3}$ M), in the presence of *t*-An (0.22 M) and $PhNEt_2$ ($4.0 \times 10^{-3}$ M) in outgassed benzene using the 337-nm pulse from a nitrogen laser produced the fluorescence of 3,9-$(CN)_2P$ (M), the 3,9-

**Table I.** Thermodynamic and Kinetic Parameters for Exciplex Exchange[a] ($S_{ex}$)

| $MQ_1$ | [b]$\lambda_{max}^{MQ_1}$, nm | $Q_2$ | [c]$IP(Q_2)$, eV | $MQ_2$ | [b]$\lambda_{max}^{MQ_2}$, nm | [d]$\Delta E$, kcal mol$^{-1}$ | [e]$k_Q\tau$, l. mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 3,10-$(CN)_2P$-*t*-An | 484 | $PhNEt_2$ | (6.94)[f] | 3,10-$(CN)_2P$-$PhNEt_2$ | 566 | 8.6 | 240 |
| 3,9-$(CN)_2P$-*t*-An | 496 | $PhNEt_2$ | (6.94)[f] | 3,9-$(CN)_2P$-PhN-$Et_2$ | 590 | 9.1 | 267 |
| 9-CNP-*t*-An | 450 | $Ph_3N$ | 6.86 | 9-CNP-$Ph_3N$ | 470 | 2.7 | 140 |
| 9-CNP-*t*-An | 450 | $PhNEt_2$ | (6.94)[f] | 9-CNP-$PhNEt_2$ | 508 | 6.8 | 31.5 |
| 9-CNP-*t*-An | 450 | $Et_3N$ | 7.50 | 9-CNP-$Et_3N$[g] | 530[h] | 9.6 | 0.4 |

[a] In benzene. [b] Corrected, precision ±2 nm. [c] Adiabatic values from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Fraxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26,** (1969). [d] $\Delta E = h\nu_{MQ_1} - h\nu_{MQ_2}$. [e] Outgassed or under $N_2$, precision ±5%. [f] Estimated from the IP of $PhNMe_2$ (7.14 eV)[c] and the effect of *N*-ethyl substituents expected from published data for aliphatic amines. [g] Very weak emission ($\phi_F{}^c \approx 2 \times 10^{-3}$). [h] Precision ±5 nm.

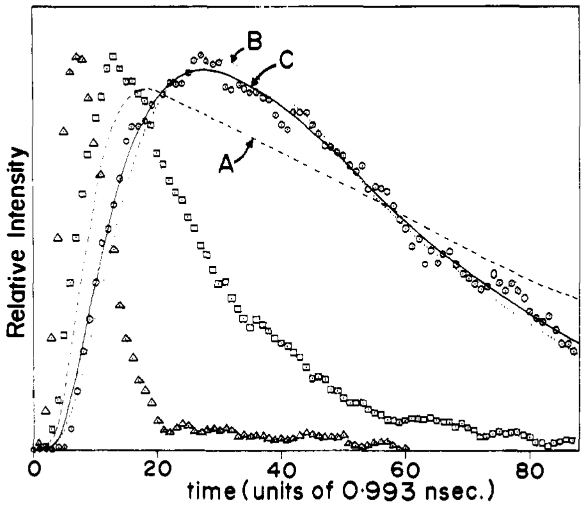

**Figure 2.** Fluorescence decay curves at 365 nm (▲), 470 nm (□), and 620 nm (⊙) in the system 3,9-(CN)$_2$P ($10^{-3}$ M), *t*-An (0.22 M), and PhNEt$_2$ ($4.0 \times 10^{-3}$ M) in outgassed benzene. Data points at 620 nm are corrected for the contribution of the 3,10-(CN)$_2$P-*t*-An exciplex at this wavelength.

(CN)$_2$P-*t*-An exciplex (MQ$_1$), and a longer-lived emission shown by time-resolved spectroscopy[4] to have the same spectral shape as the 3,9-(CN)$_2$P-PhNEt$_2$ exciplex (MQ$_2$). These three emissions were monitored at 365 (pure M), 470 (pure MQ$_1$), and 620 nm, respectively (Figure 2). The long wavelength emission was incompletely resolved spectrally from MQ$_1$, but subtraction of the calculated modest MQ$_1$ contribution at 620 nm afforded the time profile of the new emission.

Using standard deconvolution techniques, and assuming a single-exponential decay, we attempted fits of the new emission to three different excitation functions: (1) M only, (2) MQ$_1$ only, and (3) a combination of M and MQ$_1$ (Figure 2). The best least-squares fit to M only is clearly unsatisfactory (Figure 2, A) and is much inferior to the fit to MQ$_1$ (Figure 2, B). The best fit (Figure 2, C) to a linear combination of M and MQ$_1$ occurs with 83 ± 9% excitation by MQ$_1$ and a lifetime determined to be 29.0 ± 2.4 ns. Since the lifetime of MQ$_2$ in the absence of anethole is 27.4 ± 2.0 ns, the spectral and lifetime comparisons strongly support the assignment of the new emission as MQ$_2$ itself and not to an excited termolecular complex[6] or *exterplex*[1b,7] (MQ$_1$Q$_2$*). The results thus require S$_{ex}$ as the major pathway for production of MQ$_2$ in the experiment above.

Steady-state data for several systems in which exciplex exchange occurs are given in Table I. As we have previously noted,[1b,2] the relative quenching efficiencies ($k_{QT}$) for a single exciplex correlate with the quencher ionization potentials. There is no obvious relationship between $k_{QT}$ values for quenching of MQ$_1$ and $\Delta E = h\nu_{MQ_1}{}^{max} - h\nu_{MQ_2}{}^{max}$, a parameter which crudely[8] approximates $\Delta H°$ for eq 2. We expect exciplex exchange to be favored for large $\Delta E$ values. Unfortunately it is experimentally difficult quantitatively to study those cases where $\Delta E$ approaches zero. Whether S$_{ex}$ results from collapse of a short-lived exterplex as intermediate or is itself an elementary process (i.e., the molecular analogue of the eternal triangle) remains to be determined.

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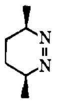
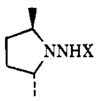
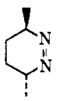
## A Stereochemical Test of Similarly Substituted Tetramethylenediazene and Cyclic Azo Decompositions in the Gas Phase at the Same Temperature

*Sir:*

Valid comparisons of stereochemical tests directed toward an understanding of the behavior of 1,4-diradicals (**1**) generated by very different methods have been complicated by the lack of examples in the literature where the type of substituents, degree of substitution, and reaction conditions have been the same. We report here the first comparison of the product compositions from similarly substituted tetramethylenediazene[1] (**2**) and six-membered cyclic azo (**3**) thermal decompositions carried out in the gas

**Table I.** Percent Yields[a]

| | *T*, °C[b] |  |  |  |  |
|---|---|---|---|---|---|
|  **(4)** | 120 | 77.6 | 5.0 | 17.1 | 0.3 |
| | 306 | 74.0 | 9.1 | 16.2 | 0.7 |
| | 439 | 72.8 | 9.3 | 15.8 | 2.1 |
|  **(8)** | 306 | 74.7 | 8.5 | 16.3 | 0.5 |
| | 439 | 72.9 | 9.7 | 16.3 | 1.1 |
|  **(5)** | 120 | 86.2 | 10.5 | 2.2 | 1.1 |
| | 306 | 79.7 | 13.1 | 6.2 | 1.0 |
| | 439 | 76.0 | 14.5 | 7.9 | 1.6 |
|  **(9)** | 306 | 80.5 | 12.7 | 5.7 | 1.1 |
| | 439 | 74.4 | 14.9 | 8.9 | 1.8 |

[a] Percent yield based on total hydrocarbon product. [b] Reactions at 120° (X = SO$_2$Ph) were carried out in *n*-octane with dry sodium methoxide for 30 min. Typical absolute yields of hydrocarbon products[11] are 38–73%. Reactions at 306 and 439° (X = SO$_2$Me) were carried out in the gas phase. Typical absolute yields of hydrocarbon products are 38–43%.