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Exciplex Quenching. Geometric and Electronic Requirements

Sir:

Much indirect evidence has accumulated for the intermediacy of excited state complexes (exciplexes) in photochemical reactions.[1] We have recently established the role of singlet exciplexes in some photocycloaddition reactions of phenanthrenes and olefins using an exciplex fluorescence quenching method.[2,3] We now report on the generality of exciplex quenching and an apparent geometrical requirement for this "termolecular" process.

The fluorescent exciplex ($\lambda_{\mathrm{emission}}$ 444 nm) formed[2] between the excited singlet state of 9-cyanophenanthrene (9-CNP) and *p*-(isobutenyl)anisole (*p*-BA) was quenched by the addition of fumaronitrile (Figure 1). A value of $k_Q\tau_{ex}^{\mathrm{air}} = 90$ was obtained by the usual Stern-Volmer analysis.[4] Other electron acceptors also quench the exciplex fluorescence; $k_Q\tau_{ex}^{\mathrm{air}}$ values from linear Stern-Volmer plots are given in Table I. The effect of air saturation on the exciplex fluorescence[2,5] intensity allows us to estimate a lifetime (τ_{ex}^{air}) of 16 nsec. Thus fumaronitrile, dimethyl fumarate, and dimethyl acetylene dicarboxylate quench the exciplex at essentially diffusion-controlled rates (Table I). Exciplex quenching experiments run at varying olefin concentrations but at constant 9-CNP concentration led, within experimental error, to identical $k_Q\tau_{ex}$ values indicating that ground-state complexation between *p*-BA and the quenchers is not important to the quenching process.

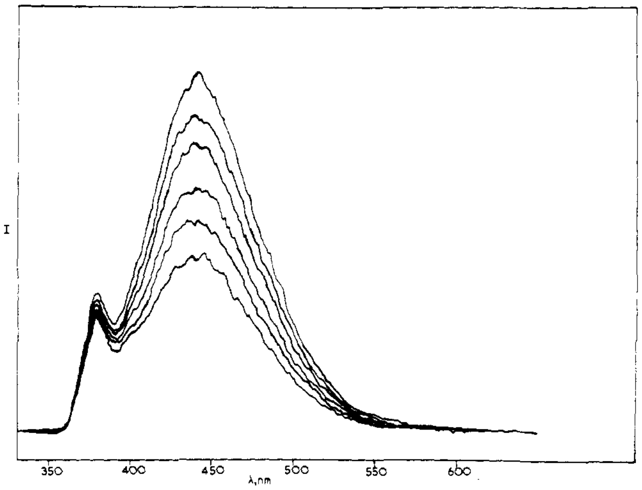
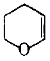
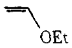
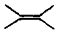
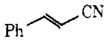
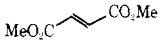
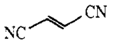


Figure 1. Quenching of 9CNP-*p*-BA exciplex by fumaronitrile: $k_Q\tau_{e}x^{\mathrm{air}} = 90\ M^{-1}$.

Table I. Rate Constants for Exciplex Fluorescence Quenching[a]

Quenchers	9CNP–*trans* Anethole 11.3 (8.0)[b]	9CNP–*p*-BA 39 (16)[b]	Anth–DEA[c] 120 (22)[b]	P–FN 23.5 (12.5)[b]
Ph_3N	1.9×10^8	1.5×10^8	—	—
Et_3N	1.5×10^8	2.0×10^8	1.4×10^7	7.0×10^9
	$<6 \times 10^6$	$<2 \times 10^6$	$<2 \times 10^5$	2.2×10^9
	$<6 \times 10^6$	$<2 \times 10^6$	—	1.6×10^8
	$<6 \times 10^6$	$<2 \times 10^6$	$<2 \times 10^5$	1.6×10^9
	1.0×10^8	8.2×10^7	1.6×10^8	
	8.1×10^9	7.6×10^9	3.3×10^9	1.4×10^8
	7.2×10^9	6.9×10^9	3.4×10^9	1.3×10^8
$MeO_2CC{\equiv}CCO_2Me$	7.7×10^9	7.6×10^9		$<4 \times 10^7$

[a] Air-saturated benzene at room temperature. Rate constants ($= k_Q\tau_{ex}^{\mathrm{air}}/\tau_{ex}^{\mathrm{air}}$). [b] Exciplex lifetimes given as $\tau_{ex}^{\mathrm{deoxygenated}}$ (τ_{ex}^{air}), in nanoseconds, estimated from the effect of aeration on exciplex emission intensity. [c] Anthracene–diethylaniline.

The results of quenching of several other exciplexes are given in Table I. Results for the phenanthrene-fumaronitrile (P-FN) exciplex[6] parallel those we have previously reported for the phenanthrene-dimethyl fumarate exciplex.[3] Where necessary, corrections were made for the simultaneous quenching[7] of monomer and exciplex and for the absorption of incident light by ground state charge-transfer (CT) complexes. The possibility that the latter leads to exciplex quenching can be ignored since the fraction of complexed quencher molecules is in all cases very small[8] (<1%). Exciplex lifetimes were obtained by the air saturation technique and were consistent (±10%) with those obtained[10] by nanosecond flash spectroscopy.

Inspection of Table I leads to several generalizations. (1) Each exciplex can be quenched to some extent by both powerful ground-state CT donors and CT acceptors. Since a CT term dominates exciplex binding, e.g., a ≫ b, c, or d for the (D,A)* exciplex in the equation below,[11] it is not surprising that further CT interaction dominates exciplex quenching.

$$\psi_{(D,A)*} = a\psi_{D^+A^-} + b\psi_{D^-A^+} + c\psi_{D*A} + d\psi_{DA*}$$

(2) Neither weak donors (ethyl vinyl ether) nor weak acceptors (cinnamonitrile) are particularly effective exciplex quenchers.

(3) Each exciplex shows a marked preference for quench-

ing either by donors (D_Q) or acceptors (A_Q). Which type of quencher is preferred can be rationalized as follows.

(a) The geometry of termolecular excited state interaction (*exterplex*[3] formation if a stable complex is involved) is predictable from simple electrostatics. Thus, a species approximately represented by $D^{\delta+}\cdots A^{\delta-}$ should be quenched from the D side by D_Q, i.e., $D_Q{}^{\delta+}\cdots D^{\delta+}\cdots A^{\delta-}$, or from the A side by A_Q, i.e., $D^{\delta+}\cdots A^{\delta-}\cdots A_Q{}^{\delta-}$. Such a geometry has been suggested[12] by Beens and Weller for the naphthalene-naphthalene-dicyanobenzene *exterplex*.

(b) Our results show a preference for quenching when the interaction occurs with the exciplex component of lower singlet energy (E_s). Thus, the $9CNP^{\delta-}\cdots pBA^{\delta+}$ exciplex clearly prefers A_Q, while the $P^{\delta+}\cdots FN^{\delta-}$ exciplex prefers D_Q. An explanation might derive from the small exciton resonance (ER) binding terms, *c* and *d*, in the equation above. We expect $c > d$ if the molecule of lower E_s acts as D, and $d > c$ if it acts as A. Since the molecule of lower E_s dominates the ER contribution interaction of the quencher with this exciplex partner might lead to more efficient quenching.

Our results suggest preliminary ground rules for exciplex quenching and thus will facilitate the use of the technique for the study of photochemical reactions proceeding through exciplexes (whether emissive or not). The photophysics of the termolecular interaction is under investigation, as are the intriguing predictions for photochemistry that derive from the $D_Q{}^{\delta+}\cdots D^{\delta+}\cdots A^{\delta-}$ and $D^{\delta+}\cdots A^{\delta-}\cdots A_Q{}^{\delta-}$ geometric models.[14]

Acknowledgment is made to the Robert A. Welch Foundation (Grant AT-532), the U.T. Dallas Organized Research Fund, and the National Science Foundation (Grant GU-4020) for financial support.

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Manganese(II) Porphyrins. Synthesis, Structures, and Preference for Five-Coordination

Sir:

Despite research on the incorporation of manganese porphyrins into several reconstituted proteins[1,2] and solution study as models for manganese chlorophylls,[3] manganese(II) porphyrins have not been definitively characterized. Our studies, motivated by the possibility of manganese(II) porphyrins acting as dioxygen carriers, reveal that previously assumed six-coordination is without substantiation. Rather, five-coordination of high-spin Mn(II) prevails. The ramifications of this stereochemical preference on our understanding of the electronically similar heme-iron stereochemistry, and reactions with dioxygen, are discussed.

Reduction of $Mn^{III}Cl(TPP)$[4] with $Cr(acac)_2$ in toluene solution affords purple crystals of the hitherto unknown four-coordinate derivative Mn(TPP)·2(toluene). Unlike its closest analogs, Mn(Pc)[5] and Fe(TPP),[6] which adopt intermediate-spin configurations with in-plane metal ions, magnetic data (μ_{eff} = 6.2 BM) and an X-ray analysis of Mn(TPP) are consistent with a high-spin configuration.

Mn(TPP) provides a good synthetic intermediate for the introduction of axial ligands. Treatment of a toluene solution of Mn(TPP) with ligand L (1-methylimidazole, 2-methylimidazole, or pyridine) gives rise to an intense green solution from which purple crystals can be isolated in high yield. Isosbestic behavior is observed in the visible spectrum throughout the ligation reaction (λ_{max} 525, 569, 605 → 533, 575, 614 nm) and, despite the use of large excesses of ligand L, only *five*-coordinate derivatives have been isolated. All solid samples have magnetic susceptibilities indicative of high-spin d^5 configurations ($\mu_{eff}{}^{25°}$ = 6.2–6.6 BM). The structure of the THF solvate of Mn(TPP)(1-MeIm) has been determined by X-ray analysis.

Diffraction data were collected on a Syntex $P\bar{1}$ diffractometer with Mo Kα radiation. The structures were solved by the heavy-atom method and refined to convergence using anisotropic temperature factors for all heavy atoms. Crystal data and refinement results are as follows: $Mn(N_4C_{44}H_{28})(C_4N_2H_6)\cdot C_4H_8O$, monoclinic; a = 27.405 (7), b = 9.645 (5), c = 17.768 (9) Å; and β = 112.45 (2)^0; ρ_{calcd} = 1.258, ρ_{obsd} = 1.27 g/cm^3; Z = 4; space group $P2_1/n$; R = 0.052 and R_2 = 0.061;[7] 5276 unique data ($F_o > 3\sigma(F_o)$, $2\theta < 52.9^0$); $Mn(N_4C_{44}H_{28})\cdot 2C_7H_8$, triclinic; a = 11.320 (6), b = 11.465 (6), c = 10.487 (6) Å; α = 110.63 (2), β = 103.34 (3), and γ , 107.80 (3)^0; ρ_{calcd} = 1.258 g/cm^3; Z = 1; space group $P\bar{1}$; R= 0.092 and R_2 = 0.068; 5659 unique data ($F_o > 2\sigma(F_o)$, $2\theta < 63.7^0$).

The structure of Mn(TPP) provides one answer to an interesting question of porphyrin stereochemistry, namely, whether independent of coordination number, a large metal ion takes an out-of-plane position from the porphinato nitrogen atoms. With one molecule per cell,[8] the point group symmetry (real or statistically effective) required of the Mn(TPP) molecule is C_i. Refinement with the Mn(II) ion positioned at the center of symmetry (center of the porphyrin molecule) leads to a Mn–N bond distance of 2.082 Å, possibly consistent with a high-spin ion.[9] However, the anisotropic thermal parameter of the Mn(II) ion, perpendicular to the mean porphinato plane, is unrealistically large (root mean square displacement 0.351 Å). An alternate refinement in which the Mn(II) ion was allowed to take an out-of-plane position, while retaining a statistical center of symmetry, leads to a slightly less unrealistic thermal parameter (root mean square 0.28, Figure 1) despite an identical *R* factor. Either alternative suggests that the Mn atom is out-of-plane in accord with theoretical calculations[10]