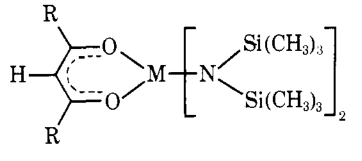
Bradley and co-workers[4] have studied the reactions of $LiN[Si(CH_3)_3]_2$ with a variety of transition metals and have prepared some interesting three-coordinate complexes. We have isolated novel four-coordinate derivatives of titanium and vanadium **3** from the reaction of 2 equiv of $LiN[Si(CH_3)_3]_2$



3

M = Ti, V
R = $C(CH_3)_3$, C_6H_5

with the appropriate diketonate complex. They are air-sensitive, highly colored crystalline solids. The mass spectra of the dipivalolylmethanato derivatives exhibit parent ion peaks. The magnetic and spectral data are consistent with the proposed structure. Several reactions of $LiN[Si(CH_3)_3]_2$ with (diket)-$CrCl_2(THF)_2$ gave brown to orange-red solutions but no products could be isolated in pure form.

We are currently examining further reactions and the chemistry of these novel diketonate stabilized organometallic and dialkylamide complexes.

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Exciplex Quenching. A Frontier Molecular Orbital Rationale

Sir:

The quenching of singlet exciplexes by electron donors or acceptors[1] has been highly useful in mechanistic dissection of photocycloadditions reactions.[2] We now report a simple frontier molecular orbital (FMO) analysis of data for quenching of a large number of exciplexes by electron donors from which order of magnitude predictions of quenching rates (k_Q) can be made for any singlet exciplex.

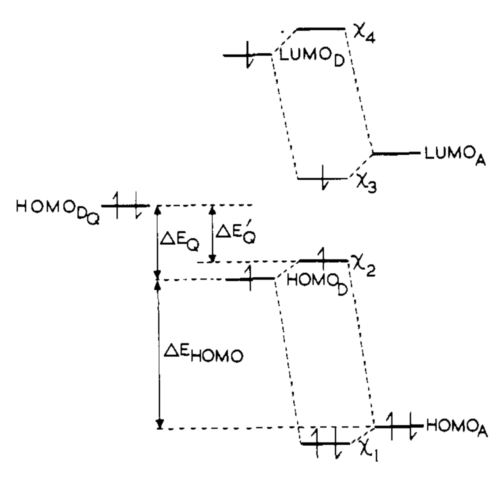

Figure 1. FMO picture of exciplex formation and quenching by an electron donor.

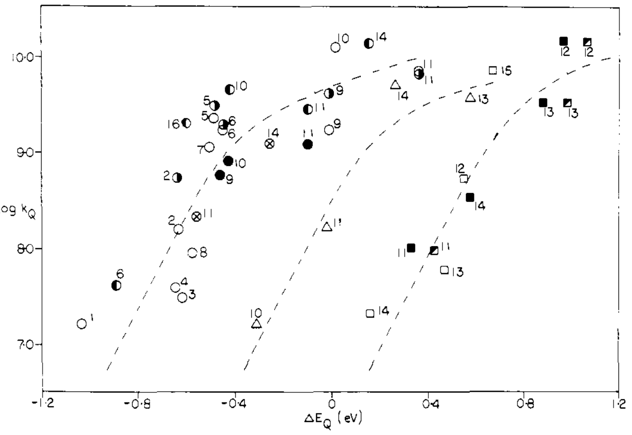

Figure 2. Log k_Q vs. ΔE_Q for quenching of exciplexes by electron donors. Exciplexes are: anthracene-FN (●), pyrene-FN (◐), P-F (◑), P-FN (○), 9CNP-PhNEt$_2$ (⊗), 3,6MeO$_2$P-9CNP (△), 9CNP-*t*-An (■), 9CNP-*p*-BA (▨), and the pyrene excimer (□). Quenchers are: (1) 2-methyl-but-2-ene, (2) ethyl vinyl ether, (3) styrene, (4) α-methylstyrene, (5) dihydropyran, (6) 2,3-dimethyl-but-2-ene, (7) β-methylstyrene, (8) anisole, (9) phenanthrene, (10) *p*-methoxy-β-methylstyrene (*t*-An), (11) triethylamine, (12) triphenylamine, (13) diethylaniline, (14) diphenylamine, (15) *N,N'*-tetramethyl-*p*-phenylenediamine, (16) diethylamine.

Table I

Exciplex	λ_{max}[c] (nm)	τ[e] (ns)	ΔE_{HOMO}[f] (eV)
Anthracene-FN	570[d]	7.5	3.74
Pyrene-FN	515	9.6	3.74
P-F[a]	480	1.4	3.37
P-FN	460	12.5	3.27
9CNP-PhNEt$_2$	489	16.8	1.46
3,6MeO$_2$P-9CNP	444	8.0	1.04
9CNP-*t*An	430	7.9	0.73
9CNP-*p*BA[b]	438	15.8	0.63
Pyrene excimer	478	16.4[g]	0.00

[a] Dimethylfumarate. [b] *p*-Butenylanisole. [c] In benzene. Corrected, ±3 nm. [d] ±10 nm. Very weak emission. [e] Air-saturated benzene. Determined either by nanosecond flash spectroscopy or from the effect of air saturation on the exciplex fluorescence intensity. [f] ΔE_{HOMO} = Ip(A) − Ip(D). [g] At [pyrene] = 5.2×10^{-2} M.

Four new exciplex orbitals χ_1, χ_2, χ_3, and χ_4 are derived from the $HOMO_D$-$HOMO_A$ and $LUMO_D$-$LUMO_A$ interactions[3] when an excited donor, D*, forms an exciplex with a ground-state acceptor, A (Figure 1). We suggest that perturbation of χ_2 by the HOMO of the quenching donor, D_Q, adequately describes the quenching. Such perturbations will be maximal when $HOMO_{D_Q}$ lies close to χ_2 in energy and should result in actual electron transfer when it is exothermic. Donor quenching efficiencies for any exciplex can, in principle, be estimated from the $HOMO_{D_Q}$-χ_2 energy gap, $\Delta E_Q'$. Since the energy of χ_2 is presently unobtainable, we assume that the energy of $HOMO_D$ approximates to that of χ_2 and calculate an alternative parameter $\Delta E_Q[Ip(D) - Ip(D_Q)]$[4]. A plot of log k_Q vs. ΔE_Q for eight exciplexes (Table I), the pyrene excimer, and 16 different quenchers is given in Figure 2. Although the data points show considerable scatter, not surprising considering the wide structural variation in donors and exciplexes, several trends are apparent: (1) Three lines adequately encompass all the data. (2) Each line shows the pronounced positive slope ($\approx$4.0 eV^{-1}) expected from a model in which the quencher acts as an electron donor.[7] Curvature seems to occur, again as expected, when k_Q approaches the diffusion limit. (3) Data points for arene-fumaronitrile (FN), phenanthrene(P)-dimethyl fumarate (F), and 9-cyanophenanthrene (9CNP)-diethylaniline ($PhNEt_2$) exciplexes cluster together and are well represented by the leftmost line. These exciplexes are quenched ($k_Q \approx 10^8$ M^{-1} s^{-1}) even when ΔE_Q is negative (≈ -0.6 eV). (4) The pyrene excimer and the 9CNP-*trans*-anethole (*t*-An) and 9CNP-*p*-butenylanisole (*p*-BA) exciplexes are far less quenchable. The single line which correlates data for these quite different complexes is shifted by about +1.0 eV from the leftmost line. These cases require positive ΔE_Q (+0.4 eV) for modest quenching rates ($k_Q \approx 10^8$ M^{-1} s^{-1}). (5) The "heteroexcimer" 9CNP-3,6-dimethoxyphenanthrene ($3,6MeO_2P$) fits an intermediate line.

The common slope for all data points suggests a common charge-transfer mechanism for both exciplex and excimer quenching.

$$\begin{aligned} D_Q + (D^{\delta+} \cdots A^{\delta-})^* &\rightarrow (D_Q{}^{\delta+} \cdots D \cdots A^{\delta-}) \\ &\rightarrow D_Q\cdot^+ + D + A\cdot^- \end{aligned}$$

Termolecular photochemistry may be expected to result from the radical ions $D_Q\cdot^+$ and $A\cdot^-$. The unsymmetrical geometries, previously demonstrated[8] for one emissive *exterplex,* and which we have suggested[1a] as being likely for the quenching interaction are easily rationalized. If D_Q is to perturb χ_2, the site of interaction should be at D where χ_2 is predominantly located.

Failure of a single line to correlate all data is, we believe, due to the failure of ΔE_Q as an approximation to $\Delta E_Q'$. We note that the exciplexes which are quenched even when ΔE_Q is negative have large ($\gtrsim$1.5 eV) $HOMO_D$-$HOMO_A$ (ΔE_{HOMO}) energy gaps. ΔE_{HOMO} is, however, small (<0.8 eV) for the group which requires positive values of ΔE_Q for efficient quenching. The single "heteroexcimer" is an intermediate case (ΔE_{HOMO} = 1.04 eV). When ΔE_{HOMO} is large ($\gtrsim$1.5 eV) exciplex binding must surely be exclusively CT with D consequently electron deficient and χ_2 located almost exclusively on it. Presumably, χ_2 is then like the HOMO of $D\cdot^+$. The essentially unit positive charge must *lower* χ_2 relative to $HOMO_D$, leading to $\Delta E_Q' \gg \Delta E_Q$ and the observation of quenching even for values of ΔE_Q down to about -1.0 eV. Since χ_2 lies *below* $HOMO_D$, we predict the excited monomer (D*) will be quenched less efficiently than the exciplex $(D\cdots A)^*$ by a given D_Q. This appears to be the case, for example, $k_Q \approx 5 \times 10^6$ M^{-1} s^{-1} for quenching of phenanthrene fluorescence by 2,3-dimethyl-2-butene whereas $k_Q = 1.6 \times 10^9$ M^{-1} s^{-1} for quenching[1a] of the P-FN exciplex by the same donor.

When ΔE_{HOMO} is small ($\lesssim$0.8 eV), χ_2 is a combination of $HOMO_D$ and $HOMO_A$ with the energy of χ_2 *above* that of $HOMO_D$ as predicted by the simple FMO model (Figure 1). Here $\Delta E_Q' < \Delta E_Q$ and the quenching is less efficient than is predicted from values of ΔE_Q. Since χ_2 lies *above* $HOMO_D$ we expect D* will be quenched more efficiently than $(D\cdots A)^*$ by a given D_Q. This also seems to be the case, for example, $k_Q \approx 5.9 \times 10^7$ M^{-1} s^{-1} for quenching of the pyrene excimer by diethylaniline whereas $k_Q = 6.2 \times 10^9$ M^{-1} s^{-1} for quenching of pyrene monomer fluorescence by the same donor.

The FMO rationale above should be applicable, mutatis mutandis, to acceptor quenching also. We have performed a few experiments with acceptors as quenchers. Correlation is hampered by the difficulty of obtaining electron affinities. The estimates obtained from Ip-Es (the singlet excitation energy) suggest $\Delta E \sim 1 \rightarrow 1.5$ eV is required for acceptor quenching at $k_Q \approx 10^9$ M^{-1} s^{-1}, but further data are required before more dependable predictions can be made.

Our results lead to reasonable predictions of donor quenching rates for *any* singlet exciplex. The utility of the exciplex quenching method for exploring the role of exciplexes in photochemical reactions is thus greatly enhanced.

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The Utilization of a Polymeric Phenylthiomethyllithium Reagent for the Homologation of Alkyl Iodides and Its Application for the Study of Intraresin Reactions of Polymer-Bound Functional Groups

Sir:

The concept that lightly cross-linked polymer matrices are perfectly rigid and inflexible is no longer acceptable. In recent years it has been demonstrated that polystyrene chains cross-linked with several percent divinylbenzene have the capability for very significant internal mobility[1] thus permitting polymer-bound functional groups to undergo intraresin reactions.[2] Nevertheless, there are a number of intriguing reports that suggest restricted interaction of polymer-bound functional groups can be achieved under certain conditions.[3] Such conditions include (1) higher levels of cross-linking,[3b,d,f] (2) very low degrees of polymer substitution,[3a,e] (3) lower reaction temperatures[3a] and, possibly, (4) the clustering of charges located near the polymer backbone.[3c] Evidence in support of the latter two factors is very limited.

We became interested in the possible role of charge clustering and temperature in controlling the interaction of polymer chains after observing the selective monooxidation of 1,7-heptanediol with a polymeric thioanisole reagent.[3c] Although the results clearly demonstrated that selective formation of the monohydroxyaldehyde increased with lower concentrations of polymer-bound functional groups, it was not possible to assess the influence of the relatively low reaction temperature or the clustering of ionic groups on the observed selectivity. Thus, temperatures approaching the glass transition temperature might be expected to result in relatively rigid polymer chains as observed in the dry state,[4] while the devel-