normal workup, a yellow oil was isolated which was recrystallized twice from hexane to give a white solid (6.2 g, 0.026 mol), mp 48–49.5 °C (lit. 52 °C).[38] IR (KBr) 1670, 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.52 (s, 3 H), 7.1–8.0 (m, 9 H); MS, *m/e* 240, 209, 163, 105.

Methyl 4-Benzoylbenzoate. Aldrich 4-benzoylbenzoic acid (4.0 g, 0.018 mol) was esterified by refluxing overnight in methanol (50 mL) containing sulfuric acid (0.5 mL). Most of the solvent was removed under aspirator pressure and water was added. The solution was made basic with K_2CO_3 and extracted with benzene. The combined benzene extract was washed with water and dried over sodium sulfate. Removal of solvent gave a white solid, which was recrystallized from hexane (3 g, 0.13 mol), mp 108–109 °C. IR (KBr) 1640, 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.88 (s, H), 7.0–8.1 (m, 9 H); MS, *m/e* 240, 209, 163, 105.

Methyl 3-Benzoylbenzoate. 3-Benzoylbenzonitrile (1.4 g, 0.0068 mol) was hydrolyzed in 50 mL of 30% alcoholic KOH according to the procedure described previously. After workup, 1 g (0.004 mol) of 3-benzoylbenzoic acid (tan solid) was obtained, which was recrystallized from MEK/hexane to give a solid, mp 161–163 °C (lit. 161–162 °C).[39] IR (KBr) 1650, 1685 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.3–8.5 (m, 9 H), 9.9 (br s, 1 H).

The ester was synthesized from 3-benzoylbenzoic acid (0.5 g, 0.003 mol) by refluxing overnight in 50 mL of methanol containing a trace of sulfuric acid, the procedure previously described for the para analogue. After similar workup and recrystallization from hexane, white crystals were obtained (~0.2 g), mp 43–45 °C. IR (KBr) 1650, 1725 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.82 (s, 3 H), 7.1–8.4 (m, 9 H); MS, *m/e* 240, 209, 163, 105.

3-(Trifluoromethyl)benzophenone. Aldrich *m*-(trifluoromethyl)benzonitrile (4.3 g, 0.025 mol) in benzene was added dropwise to an ether solution containing 0.03 mol of phenylmagnesium bromide; the mixture was refluxed for 2 h. Dilute HCl/ice water was added and the layers were separated. The organic layer contained mostly unreacted bromobenzene. The aqueous layer was heated on the steam bath for 2 h followed by cooling and extraction with ether. The combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent gave the crude product; recrystallization from hexane gave white crystals (1.4 g, 0.006 mol), mp 49–51 °C. IR (KBr) 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.2–8.0 (m); MS, *m/e* 250, 173, 145, 105 (base), 77.

Irradiation and Analysis Procedures. These were conducted as in earlier studies.[9] Most substituted acetophenones for calibrating GC responses were avaliable commerically. Ones which were not were assumed to respond the same as their isomers to FI detectors. Type II products were identified by their GC retention times on column containing either 4% QF-1 and 1% Carbowax 20 M on Chromosorb G or 5% FFAP on AW-Chromosorb P. Hexadecane was used to measure acetophenone concentration, and eicosane, docosane, or tetracosane were used for the substituted ketones. Pentadiene isomerization was monitored on a 25-ft column containing 25% 1,2,3-tris(2-cyanoethoxy)propane. Infotronics digital intergrators were used to measure product/standard peak area ratios.

Samples were irradiated in degassed and sealed 13 × 100-mm Pyrex tubes in a "merry-go-round" apparatus.[40] The 313-nm band of an Hanovia 450-W mercury arc was isolated with an alkaline $KCrO_4$ filter solution.

UV spectra were recorded on a Cary 219 spectrophotometer. Phosphorescence spectra were recorded on 10^{-4} M solutions on a Perkin-Elmer MPF-44A spectrofluorimeter with a phosphoroscope. Reduction potential were measured relative to SCE at a hanging mercury drop electrode by cyclic voltammetry with a PAR 174A analyzer. With 10^{-4} M acetonitrile solutions, half-wave potentials were independent of sweep rate between 100–500 mV/s.

Acknowledgment. This work was supported by NSF Grants CHE76-11892 and CHE79-10831. It is a great pleasure for the senior author (P.J.W.) to wish George Hammond a happy birthday, for it was in George's laboratory that we began these kinds of photochemical experiments.[41]

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Communications to the Editor

Regioelectronic Control of Intramolecular Charge-Transfer Quenching in Excited Triplet *p*-Acylbenzoate Esters

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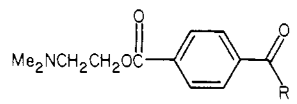
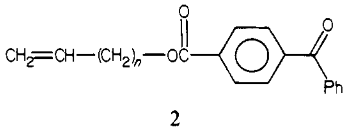
It is now widely recognized that charge-transfer (CT) interactions are the most common cause of excited-state quenching.[1] The kinetics of CT quenching and exciplex formation are usually correlated with the thermodynamics for full electron transfer.[2,3] With the close orbital overlap required for exciplex formation, steric effects often make such correlations rough.[3,4] Another important factor in CT interactions should be the accessibility of the donor orbital to the appropriate acceptor orbital. Small rate variations in several systems have already been interpreted as proof of this factor's importance.[5,6] We now report that electronic configuration is also a major factor.

The best test of the importance of orbital accessibility is provided by bifunctional molecules in which overlap between donor and acceptor orbitals is limited by the connecting skeleton's flexibility. We find a huge difference in intramolecular quenching rates depending on whether the excited acceptor has an n,π^* or π,π^* configuration, the first report of any significant configurational effect on CT quenching. The molecules of interest are the β-(dimethylamino)ethyl esters of *p*-benzoyl- and *p*-valerylbenzoic acid.



1-B, R = Ph
1-V, R = $CH_2CH_2CH_2CH_3$
1-A, R = CH_3



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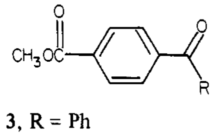

3, R = Ph
4, R = $CH_2CH_2CH_2CH_3$

[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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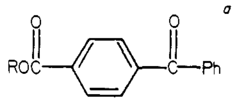
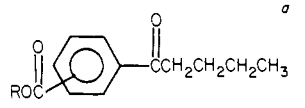
Table I. Phosphorescence of



R	$\lambda_{0,0}$, nm	Φ_p^{rel}	τ_p, μs[b]
CH_3	437	1	130[c]
$Me_2NCH_2CH_2$	440	0.08	10

[a] 10^{-4} M ketone in degassed CCl_4 at 25 °C. [b] Determined by quenching with 2,5-dimethyl-2,4-hexadiene. [c] Reference 7 reports a 100-μs lifetime measured by flash spectroscopy.

Table II. Photochemistry of



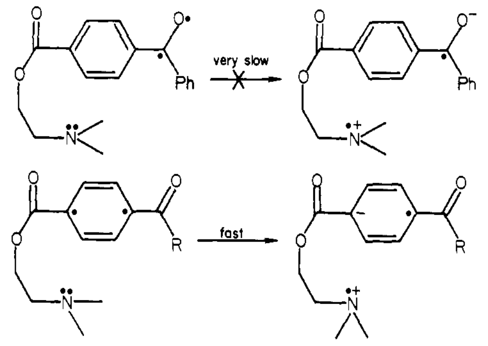
position	R	Φ_{II}[b]	$1/\tau_T$,[c] 10^8 s^{-1}	k_H	k_{CT}
para	CH_3	0.19	1.2 ± 0.1	1.2	
para	CH_3[d]	0.60	1.6 ± 0.1	1.6	
para	$Me_2NCH_2CH_2$	0.06	5.0 ± 0.3	1.2	3.8 ± 0.4
para	$Me_2NCH_2CH_2$[d]	0.13	6.7 ± 0.4	1.6	5.1 ± 0.5
para	$Me_2NCH_2CH_2CH_2$[d]	0.11	8.2 ± 0.3	1.6	6.6 ± 0.5
meta	CH_3	0.23	2.8 ± 0.2	2.8	
meta	CH_3[d]	0.90	4.8 ± 0.3	4.8	
meta	$Me_2NCH_2CH_2$	0.16	2.9 ± 0.2	2.8	
meta	$Me_2NCH_2CH_2$[d]	0.32	4.2 ± 0.3	4.2	

[a] 0.01–0.10 M ketone in degassed benzene at 25 °C. [b] Acetophenone 1-A formation, extrapolated to infinite dilution. [c] Determination by Stern-Volmer quenching with dienes, extrapolated to infinite dilution. [d] In acetonitrile containing 2% water.

Compound **1-B** is similar to those studied by Winnik, who has reported that triplets of structure **2** do not undergo internal quenching by the remote double bond unless $n \geq 8$.[7] Excited ketones are known to undergo facile CT quenching by alkenes.[6,8] Since shorter chains do not allow the double bond to reach the carbonyl group, these results demonstrate that the locus of electron deficiency in n,π* excited benzophenones is the carbonyl n orbital. In analogy with this earlier work, we did not expect **1-B** to show significant internal quenching if the lone pair orbital on nitrogen must overlap with the half-empty n orbital on oxygen in the n,π* triplet.

Table I compares phosphorescence behavior for **1-B** and the model methyl ester **3**. The triplet lifetime of **3** is the same as that measured by Winnik.[7] The decrease in the emission intensity of **1-B** parallels the decrease in its triplet lifetime, both relative to **3**. Triplet **1-B** clearly is being quenched by the tertiary amines present in solution. Little of the quenching is bimolecular; the phosphorescence quenching produced by addition of varying amounts of β-(dimethylamino)ethyl benzoate to solutions of **3** indicated a bimolecular quenching rate constant of 1×10^8 M^{-1} s^{-1}. The bimolecular quenching contribution to $1/\tau$ in **1-B** is thus only 1×10^4 s^{-1}. Therefore, we can conclude that the rate of intramolecular CT quenching in triplet **1-B** is 1.0×10^5 s^{-1}. This low value contrasts with values $>10^9$ s^{-1} for β-, γ-, and δ-amino ketones[9] and supports the simple view that the half-vacant n orbital is almost totally localized on the carbonyl oxygen *in terms of chemical reactivity*. These results provide even stronger evidence than Winnik's, because amines are much better donors than alkenes. For example, triplet benzophenone undergoes CT quenching by 3 M triethylamine in 10 ps![10]

Scheme I



As we report separately,[11] alkyl aryl ketones such as **1-V** have π,π* lowest triplets. Consequently, the half-vacant acceptor orbital is a π orbital localized heavily on the benzene ring in a position readily accessible to the donor lone pair. Table II compares the photochemistry of **1-V** and the model methyl ester **4**, both of which undergo Norrish type II elimination[12] to yield the respective acetophenones. The type II quantum yield and triplet lifetime of **1-V** both decrease with increasing **1-V** concentration because of bimolecular quenching as with **1-B**. The values recorded in Table II are those extrapolated to infinite dilution and are 4–5 times lower than the corresponding values for **4**. The presence of the amino group in **1-V** clearly causes a rapid internal quenching process with a rate constant of 5×10^8 s^{-1}. This internal quenching apparently does not lead to photoreduction products since the quantum yield for ketone disappearance extrapolates to zero for **1-A**. The homologue of **1-V** with one additional methylene separating the amine from the benzene ring undergoes slightly faster internal quenching. As Table II indicates, the rate of the quenching process does not vary much with solvent polarity.

We ascribe the quenching to exciplex or radical-ion pair[10] formation. The triplet reduction potential of **1-V** is −33 kcal/mol (relative to SCE).[13] Since tertiary amines have oxidation potentials of +34 kcal,[14] internal electron transfer in triplet **1-V** is thermoneutral. Electron transfer is always rapid in such cases when appropriate orbital overlap is possible.[15]

Besides the large body of evidence that benzophenones and phenyl alkyl ketones normally have identical chemical reactivities,[16] several facts indicate that the difference between **1-B** and **1-V** is due only to their different triplet configurations. As in our earlier studies of amino ketones,[9] there is no spectroscopic evidence for ground-state amine–ketone interactions in **1-B** or **1-V**. Triplets **3** and **4** are quenched by triethylamine with the same large rate constant (5×10^9 M^{-1} s^{-1} in benzene); this fact reflects the nearly identical triplet-state reduction potentials of **3** and **4** (and thus of **1-B** and **1-V**)[17] and indicates that all acceptor orbitals become accessible to the donor orbital during a prolonged bimolecular solution encounter. Finally, the meta isomer of **1-V** (**5**) shows the same triplet lifetime as the meta isomer of **4**, corresponding presumably to the same rate of γ-hydrogen abstraction in both. Like **1-B**, **5** has an n,π* lower triplet[10] and like **1-B** undergoes no measurable internal quenching.

Scheme I depicts the difference between **1-B** and **1-V** in terms of common valence bond structures of the n,π* and π,π* triplets. The ^3L_a states of substituted benzenes are complex mixtures of configurations; the picture in Scheme I emphasizes that the half-vacant π orbital of **1-V** is largely localized on the benzene ring and that the triplet resembles a 1,4-biradical.[11,18] The

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resulting exciplex does not have a charge distribution which would encourage α-proton transfer from the amine radical-cation center.[19]

Although these results dramatically illustrate the different acceptor orbital locations of n,π* and π,π* triplets, it is difficult to assess the individual k_{CT} values quantitatively. Since there apparently is a nearly 50:50 mixture of n,π* and π,π* triplets in **1**-V,[11] the actual rate constant for a π,π* triplet is $\sim 1 \times 10^9$ s^{-1}. This value is comparable to that in δ-(dialkylamino)valerophenones,[9] an interesting and somewhat surprising fact. Although in both cases there are four connecting atoms between the nitrogen donor and the excited acceptor, the conformational preferences of the ester group[20] might have been expected to destabilize a cyclic conformation such as pictured in the scheme.

In summary, the specific probe afforded by intramolecular bifunctional photochemistry reveals that there is a vast difference between n,π* and π,π* triplets in the position at which donor orbitals can feel sufficient overlap for rapid electron-transfer interactions. More generally, these results strongly support the concept of HOMO and LUMO orbital overlap in electron-transfer reactions. We are currently studying internal quenching in other amino ketones to assess the generality of these conclusions.

Acknowledgment. This work was generously supported by NSF Grant CHE-79-10831.

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Photoinduced Elimination of H_2 from $[Pt_2H_3(dppm)_2]PF_6$ and $[Pt_2H_2Cl(dppm)_2]PF_6$[†]

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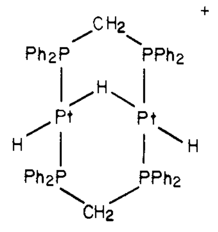
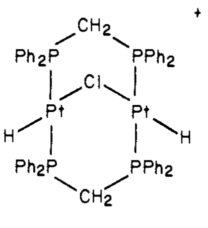
Photolysis of *monomeric* di- and polyhydride transition-metal complexes has generally been found to give elimination of H_2 as the dominant photoreaction.[1-3] The question arises as to whether or not H_2 elimination will occur from *di-and polynuclear* hydride complexes in which the hydride ligands are bound to different metals or bridge two or more metal centers. Such dinuclear elimination reactions could be important in solar energy conversion schemes using soluble complexes for producing H_2 from H_2O.[4-6] The few polynuclear hydridocarbonyl cluster complexes which have had their photochemistry examined do not show H_2 loss but instead either CO loss or metal–metal bond cleavage.[7-10] In search of such H_2 elimination reactions we have examined the dinuclear hydride complexes $[Pt_2H_3(dppm)_2]PF_6$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) and $[Pt_2H_2Cl(dppm)_2]PF_6$ (**2**), both of which have been well characterized by Brown, Puddephatt, and co-workers.[11-13] The studies reported herein show that both of these complexes readily lose H_2 upon photolysis and demonstrate the feasibility of such reaction from di- and polynuclear hydride complexes.[14]



1



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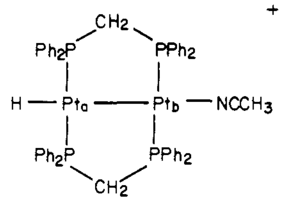
Degassed acetonitrile solutions of **1** show little or no decomposition upon prolonged heating at 80 °C, but photolysis ($\lambda \geq$ 300 nm) of thoroughly degassed CH_3CN solutions of $[Pt_2H_3(dppm)_2]PF_6$ gives visible gas evolution and a rapid change from colorless to red. The UV–VIS spectral changes which occur are shown in Figure 1, and the maintenance of the isosbestic points at 337 and 372 nm indicates a clean conversion to products. The red color arises as a result of the weak visible absorption by the photoproduct (ϵ_{450} 130 M^{-1} cm^{-1}). One mole of H_2 per mole of complex irradiated is rapidly evolved ($\sim$30 min), although prolonged photolysis (>48 h) leads to secondary photochemical reactions and further slow evolution of H_2. A total of 1.42 mol of H_2 were evolved in one 66-h experiment. Concentration and cooling of CH_3CN solutions irradiated to the point of evolution of 1 mol of H_2 give a red solid which has been characterized as $[Pt_2H(CH_3CN)(dppm)_2]PF_6$.[15] The reaction shown in eq 1 is

$$[Pt_2H_3(dppm)_2]^+ + CH_3CN \xrightarrow{h\nu} H_2 + [Pt_2H(CH_3CN)(dppm)_2]^+ \quad (1)$$

thus indicated and spectroscopic data imply structure **3** for the photoproduct. The IR spectrum of **3** shows a ν_{Pt-H} vibration at



3

2033 cm^{-1}, indicative of a terminal rather than bridging hydride, and a weak ν_{CN} stretch at 2258 cm^{-1}. The hydride resonance in the ^{1}H NMR spectrum of **3** in CD_3CN solution appears at δ −8.9 as a pseudoquintet due to coupling to the four ^{31}P nuclei ($^2J_{P-H}$, $^3J_{P-H}$ = 9 Hz) with two sets of $^1/_4$ intensity satellites from coupling to the two inequivalent ^{195}Pt atoms ($^1J_{Pt_a-H}$ = 975 Hz; $^2J_{Pt_b-H}$ = 73 Hz). As Puddephatt has shown,[16-18] this satellite pattern is

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

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(14) Photoinduced elimination of H_2 from *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma,\eta\text{-}C_5H_4)_2]$ and from $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ has also been implicated but few details were given. The mechanism suggested for the latter involved an intermediate with both hydrides on one metal as the light-absorbing species from which H_2 loss occurred (Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J., *J. Chem. Soc., Dalton Trans.* **1980**, 29).

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