18 H), 1.55–1.95 (br, partly covered by solvated residues), 1.4 (br s, 70–74 H); ^{13}C NMR (fluoride salt, D_2O) δ 136.0, 135.7, 132.5, 132.2, 65.4, 64.2, 63.9, 61.7, 61.0, 51.2, 50.9, 29.9, 29.8, 27.9, 27.7, 23.8, 23.7, 23.6.

The minor component exhibited a ^{1}H NMR spectrum which was virtually identical with the corresponding spectrum of **5** except for one feature: in addition to the signal of the N–CH_3 groups at 2.89 ppm another singlet at 3.03 ppm appeared having one-fifth of the area of the peak at 2.89. We tentatively assign the structure of a mono-in N–CH_3 isomer to this compound.

Acknowledgment. This work was supported by a grant from Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie. I thank H. Oswald for competent technical assistance.

Effect of Phenyl Substitution on the Photochemistry of Conformationally Restricted Cycloalkanones[1]

H. L. Casal,[†] W. G. McGimpsey,[†] J. C. Scaiano,*[†] R. A. Bliss,[‡] and R. R. Sauers*[‡]

Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6, and the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. Received April 22, 1986

Abstract: The photochemical and photophysical properties of pentacycloundecan-8-one (**1**) and the phenyl derivatives **2** and **3** are described. All three systems are highly photostable in both singlet and triplet manifolds. No fluorescence from the aromatic moieties in **2** and **3** was observed; they appear to undergo rapid intramolecular energy transfer to the carbonyl chromophores. Whereas at 298 K the excited state behavior of the carbonyl group in **2** ($\Phi_f = 0.0033$, $\tau_s = 11.1$ ns, $\tau_T = 12$ ns) is consistent with that of **1** ($\Phi_f = 0.0039$, $\tau_s = 10.9$ ns, $\tau_T = 9.4$ ns), the syn-isomer **3** is nonfluorescent and has a shorter triplet state lifetime (3.6 ns). Rapid internal exciplex formation is believed to be responsible for this behavior.

The photochemical and photophysical behavior of nonconjugated polychromophoric molecules has continued to be the subject of intense investigation by many groups. These studies have revealed novel photochemical phenomena and have provided information on intramolecular energy transfer,[2-5] electron, charge transfer, or exciplex formation,[6-13] and energy migration.[14] Complex behavior is expected in bichromophoric systems not only because of competitions among the above-mentioned processes but also because more than one mechanism may be operative.[6,7,15-19]

For example, it has been known for some time that β-aryl rings "deactivate" both carbonyl singlets and triplets as evidenced by decreased intersystem crossing efficiencies and reduced quantum yields of Norrish type II reaction.[11-13,15-19] In fact, the low efficiency of photoreduction of β-phenylpropiophenone has been recognized for over 40 years.[19] In at least one study it was concluded that chromophoric coupling occurs "through space" rather than "through bonds" and that interaction of both n_{CO} and π_{CO} with the π-aryl system may be of importance.[15] In agreement with this, limitations to conformational mobility (e.g., by inclusion in zeolites) are frequently sufficient to limit severely the efficiency of intramolecular deactivation.[20-22]

In a different context Amrein and Schaffner[4] have rationalized the behavior of isomeric naphthyl indanones in terms of competing through space exciplex formation (endo isomer) and through bond energy transfer (exo and endo isomers). These workers postulated that through σ-bond interaction is of greater importance than through-space orbital overlap in the endo case and that weak intramolecular exciplex formation provides an endo-specific mechanism for radiationless deactivation.

We have been interested in the geometrical aspects of these kinds of long-range phenomena in bichromophoric systems, especially in nonconjugated unsaturated ketone photochemistry.[23] This report deals with intramolecular interactions which control the behavior of nonconjugated phenyl ketones. Earlier studies have dealt with aromatic ring quenching of carbonyl triplet states in intermolecular systems[24-29] and in relatively flexible β-aryl ketones.[11-19] We sought to design molecules with greater molecular rigidity in which exciplex lifetimes might be lengthened. This

Table I. Absorption Spectra of **1**–**3** in Acetonitrile Solution

substrate	λ_{max} (ε)[a]	λ_{max} (ε)[a]
1		299 (18)
2	258 (210)	299 (20)
3	262 (246)	301 (33)

[a] λ_{max} in nanometers (±2) and ε in units of M^{-1} cm^{-1}.

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[‡] Rutgers.

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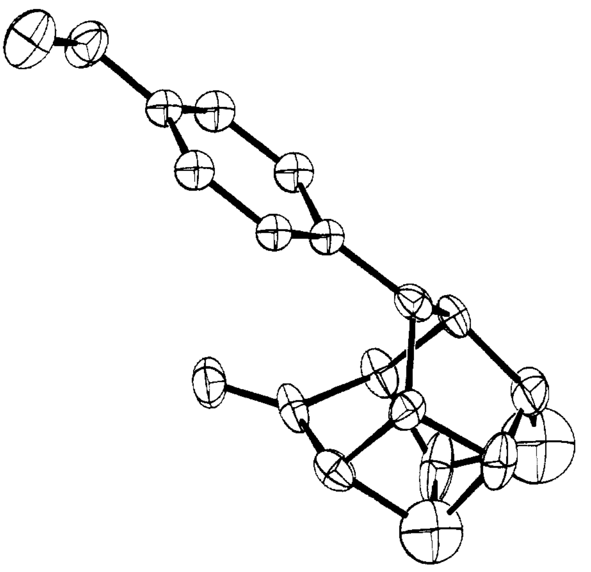


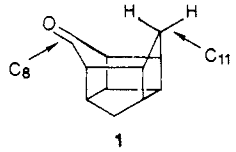
Figure 1. ORTEP drawing showing the structure of the p-methoxy derivative of **3**.[30]

Table II. Fluorescence Data in Acetonitrile at 298 K[a]

substrate	λ_{ex}/nm	Φ_F	λ_{max}/nm	τ/ns
1	300-310	0.0039	430	10.9
2	300-310	0.0033	435	
3	300-310	$\ll$0.0005		
2	262-268	0.0032	436	11.1
3	262-268	$\ll$0.0005		

[a] In 2-methylbutane:cyclopentane at 77 K. Both **2** and **3** exhibited fluorescence emission: $\lambda_{max} \sim$ 425-430 nm.

paper deals with a series of 11-phenylpentacycloundecan-8-ones (**1**-**3**) for which we have evaluated various photochemical and photophysical properties.



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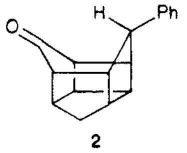

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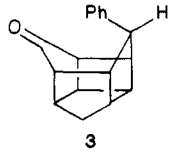
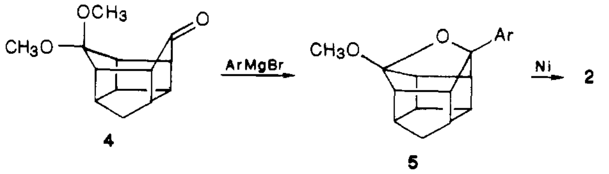


3

Results

Synthesis and Structure. A key starting material for **2** and **3** as well as for other aryl derivatives is the ketal **5**, prepared as described in an earlier study by addition of the appropriate Grignard reagent to **4** (eq 1).[23] The anti derivative (**2**) was obtained from **5** with use of Raney nickel by a modification of our earlier procedure. The structure of **2** was assigned by analysis of the ^{1}H NMR spectrum which showed a singlet at δ 3.1 attributable to the benzylic proton at C_{11}. The syn derivative (**3**) was obtained by conversion of **5** to the bromide **6** with use of HBr followed by Raney nickel hydrogenolysis (eq 2). In accord with expectations based on the magnitude of the dihedral angles with the neighboring protons (~80°), the benzylic proton appeared as a triplet (J = 3 Hz). Final confirmation of the structures is provided by single-crystal X-ray crystallographic analyses which were done on the corresponding p-methoxy derivatives.[30] Figure 1 shows an ORTEP drawing for the methoxy derivative of **3**, illustrating the proximity between the aromatic π system and the carbonyl center.

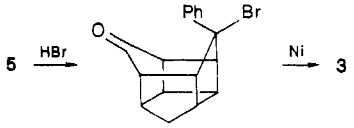


(1)

Table III. Kinetic Parameters for Triplet Decay in Isooctane

substrate	τ_T^{300K}/ns	E_a/kcal mol^{-1} [a]	log (A/s^{-1})[a]	T range (K)
1	9.4[b]	5.34 ± 0.20	11.94 ± 0.25	173-247
2	12	4.88 ± 0.36	11.49 ± 0.52	178-304
3	3.6[b]	5.58 ± 0.52	12.52 ± 0.39	184-217

[a] Errors quoted as $\pm 2\sigma$. [b] Extrapolated; note also the rather limited temperature range in which the experiment could be carried out.



(2)

UV-Absorption Spectra. The absorption maxima in the UV spectra of **1**-**3** are given in Table I, which illustrate (judging from the extinction coefficients) that there may be some weak interactions between the two chromophores in the syn compound (**3**) but not in the anti (**2**).

Fluorescence Spectra and Quantum Yields. Fluorescence spectra were recorded at several concentrations and at two different excitation wavelengths chosen to excite the aryl and carbonyl chromophores separately. These results are summarized in Table II.

Quite clearly the fluorescence in the anti isomer, **2**, arises almost exclusively from the carbonyl group regardless of the excitation wavelength. Because the quantum efficiency is independent of concentration (0.001-0.02 M) we infer that intramolecular energy transfer from the aryl groups ($E_s \sim$ 102-105 kcal/mol) to the carbonyl groups ($E_s \sim$ 85 kcal/mol) occurs with over 95% efficiency.

No fluorescence ($\Phi_f \ll 0.0005$) could be detected from solutions of **3** at room temperature; however, at 77 K with a 4:1 mixture of 2-methylbutane:cyclopentane as solvent (this solvent mixture is liquid at 77 K), both the syn (**3**) and anti (**2**) isomers showed fluorescence emission at λ_{max} 425-430 nm. The intensity of fluorescence for **3** is approximately one-half of that for **2**. This result is consistent (vide infra) with the observation that **3** undergoes some intersystem crossing at low temperature (-60 °C) and suggests that the intramolecular processes leading to the deactivation of singlet **3** may become inactive at these temperatures, thus allowing other processes, such as fluorescence and intersystem crossing, to compete.

Fluorescence Lifetimes. Lifetime measurements were carried out with use of time correlated single photon counting. Selective excitation at the carbonyl band (λ_{ex} = 300-310 nm) and monitoring carbonyl emission (λ_{em} > 400 nm) led to fluorescence lifetimes of 11.8 and 12.3 ns for **1** and **2** in cyclohexane, respectively. In acetonitrile the corresponding values were 10.9 and 11.1 ns for **1** and **2**, respectively. The lifetimes for **2** were independent of whether the excitation wavelength is ~300 or ~262 nm, indicating that energy transfer from the aromatic moiety to the carbonyl group is extremely fast; the intensity of luminescence

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(30) The methoxy compounds were prepared by the same methods as **2** and **3** and showed analogous spectral data; R. Bliss, unpublished results. Full details of the X-ray crystallographic analysis will appear in *Acta Crystallogr.*

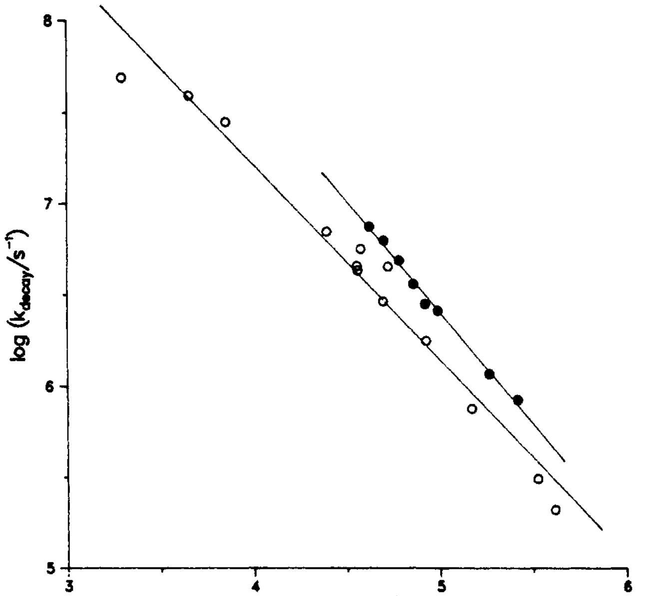

Figure 2. Temperature dependence of the decay rate constants ($k_{decay} = \tau_T^{-1}$) for **2** (○) and **3** (●) in isooctane.

is, however, higher when $\lambda_{ex} \sim 262$ nm, reflecting the better absorption characteristics in this spectral region.

Attempts to measure the fluorescence lifetime of **3** at room temperature were unsuccessful, as expected, since no fluorescence ($\Phi_f \ll 0.0005$) was detected for **3** (except at 77 K).

Laser Photolysis Studies of the Triplet State. Direct excitation of **1**–**3** in isooctane with use of the pulses (308 nm) from an excimer laser produced the corresponding triplet states which were monitored at low temperature (where the lifetimes were sufficiently long). No signals that could be attributed to an exciplex and/or biradical could be detected.

Triplet lifetimes were monitored at 290 nm and led to the parameters given in Table III (see Figure 2). Quenching experiments with biphenyl, in which the formation of triplet biphenyl was monitored, confirmed the assignment of the signals observed to the corresponding carbonyl triplets.

Stern–Volmer studies of the yield of biphenyl were carried out at –60 °C in isooctane in order to confirm the assignment at this temperature and to estimate the triplet yields from ketones **2** and **3**. The details of this technique are the same as in the literature;[31] briefly, samples of matched optical density (at 308 nm) of **2** and **3** were examined in the presence of various concentrations of a quencher capable of producing an easily detectable triplet signal (such as biphenyl). The reciprocal of the biphenyl triplet yield (monitored as the triplet absorption at 365 nm, A_{365})[32] is then plotted against the reciprocal of the quencher concentration. The plot yields $k_q\tau_T$ from the intercept-to-slope ratio, while the intercept is proportional to the reciprocal of the quantum yield for intersystem crossing, Φ_{ISC}, i.e.,

$$\frac{1}{A_{365}} = \frac{\alpha}{\Phi_{ISC}}\left(1 + \frac{1}{k_q\tau_T[\text{biphenyl}]}\right)$$

where α is a constant relating A_{365} and the quantum yield of biphenyl triplet.

These experiments led to $k_q\tau_T$ values of 98 and 60 M^{-1} for **2** and **3**, respectively (at –60 °C). Combining this with the decay data in Table III leads to an average k_q value of $\sim 3.2 \times 10^8$ M^{-1} s^{-1} for biphenyl at –60 °C, a very reasonable value for this rate constant at this temperature.[33]

The ratio of intercepts yields

$$\Phi_{ISC}^3/\Phi_{ISC}^2 \sim 0.13 \text{ (at –60 °C)}$$

Table IV. Phosphorescence Spectra and Lifetimes at 77 K

substrate	media^a	λ_{ex}/nm	λ_{em}/nm^b	τ/ms^c
1	MCH	300	464	0.33
	IP:CP	300	465	0.28
2	MCH	262	458	0.30
	IP:CP	262	465	0.25
	IP:CP	300	463	
3	MCH	262	467	0.53
	IP:CP	262	465	
	IP:CP	300	464	0.52

^{a}MCH = methylcyclohexane; IP:CP = 4:1 2-methylbutane:cyclopentane. ^{b}At the maximum, ±2 nm. ^{c}Typical error, ±0.05 ms.

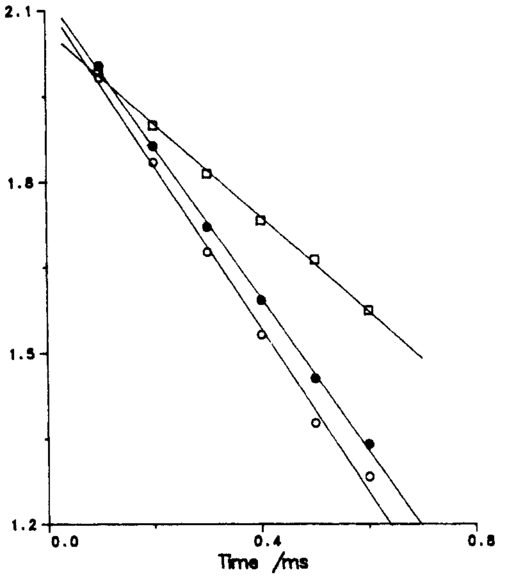

Figure 3. Representative first-order decays of the phosphorescence from **1** (●), **2** (○), and **3** (□) in a methylcyclohexane glass at 77 K. The excitation wavelength was 262 nm for **2** and **3** and 300 nm for **1**.

Phosphorescence at 77 K. The phosphorescence spectra and lifetimes of **1**–**3** were recorded at 77 K with two different excitation wavelengths in methylcyclohexane and 4:1 2-methylbutane:cyclopentane; the results are summarized in Table IV. In all cases the spectra were featureless. Emission maxima for **2** and **3** were identical for excitation at both 262 and 300 nm. In 2-methylbutane:cyclopentane, which is a liquid at 77 K, the emission maxima for **2** and **3** were in the same position as that for **1**, indicating that the carbonyl group is responsible for the phosphorescent properties.

The phosphorescence decays at 77 K followed monoexponential behavior in both the liquid and glass systems, with typical lifetimes in the submillisecond time scale (Table IV and Figure 3). The lifetime of **3** was roughly twice as long as those for **1** and **2**, suggesting that under these conditions the *syn*-phenyl ring in **3** provides some protection for the carbonyl chromophore.

Photochemical Stability. Compounds **1**–**3** were shown to be stable (by ^{1}H NMR and GC/MS analysis) to long-term irradiation at both 310 and 254 nm. Norrish type I cleavage might have been expected followed by decarbonylation or oxacarbene formation. We can only infer that these processes, if viable, are reversible. Although **1**–**3** contain γ-hydrogens (benzylic in the

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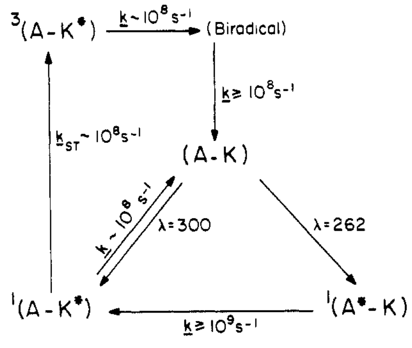
(33) For the quenching of propiophenone triplets by 1-methylnaphthalene the rate constant is 3.8×10^9 M^{-1} s^{-1} under the same experimental conditions. However, biphenyl is known to be a less efficient quencher than more rigid energy acceptors: Scaiano, J. C.; Leigh, W. J.; Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806.

Scheme I. Photochemistry of **2** at 298 K

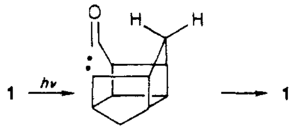


cases of **2** and **3**) we found no evidence for the Norrish type II process.

Discussion

The results obtained in this investigation are broadly consistent with the conclusions reached by Amrein and Schaffner,[4] but the contrast in behavior between the syn and anti derivatives is, in fact, even greater in our systems. Thus, in the syn system (**3**) we find evidence for "through space" enhancement of radiationless decay processes for aromatic singlet states, as well as carbonyl singlet and triplet states.

The photostability of **1**–**3** is rather remarkable, particularly in view of their very short triplet lifetimes. In particular, in the case of **1**, it is difficult to see how nonreactive decay pathways could lead to a short triplet lifetime such as that given in Table III. A more likely explanation is that triplet **1** undergoes a Norrish type I cleavage (eq 3) to yield a short-lived biradical, **7**, which regenerates **1**.[34]

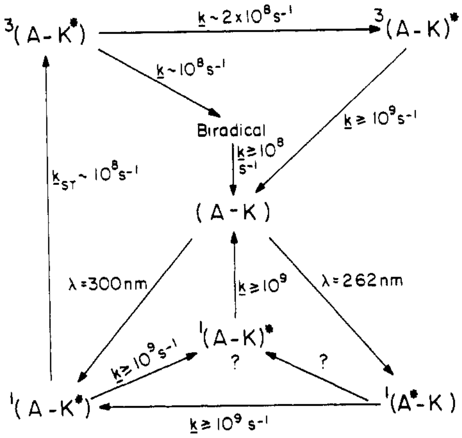


(3)

7

We have recently shown that biradicals derived from cyclopentanones have lifetimes of ~10 ns.[35] In the case of **7** the lifetime is likely to be even shorter as a result of the forced proximity of the two radical sites.[36] We assume that the biradical is short lived and leads quantitatively to the regeneration of **1**. No evidence for the Norrish type II reaction is observed from products or time-resolved studies; the O···H$_{11}$ bond distance (~3.15 Å)[41] must be too large to permit abstraction, while C···H$_{11}$ abstraction at ca. 2.60 Å would not be energetically favorable.[42,43]

Scheme II. Photochemistry of **3** at 298 K



Our observations and conclusions for ketone **2** and **3** are summarized in Schemes I and II in which the notation A–K represents the aryl ketones in their ground states. The site of excitation is denoted by an asterisk on the appropriate chromophore.

While **3** does not show any direct evidence for singlet energy transfer from excited aryl rings to carbonyl (k^s_{ET}), we prefer this decay route by analogy to the behavior of the anti system (vide infra). The absence of aromatic fluorescence is, of course, indicative of a short lifetime for the excited chromophore.

The fact that the fluorescence spectra for **2** are identical, regardless of the chromophore excited, supports the idea that singlet energy transfer from the aryl group to the carbonyl group is a very rapid process (i.e. $>10^9$ s^{-1}).

The decay of singlet **3** must involve extensive quenching by the phenyl ring, since no fluorescence from **3** can be detected at room temperature. The rate of intramolecular deactivation must exceed 10^9 s^{-1}. This contrasts with flexible systems such as those examined by Whitten et al. where fluorescence is readily detectable. For example, 4-methyl-4-phenyl-2-pentanone has an estimated singlet lifetime of 4.5 ns in benzene.[15]

Efficient triplet deactivation via interaction with the phenyl ring is evident in the case of **3**, where the triplet lifetime at room temperature is 3.6 ns compared with 12 ns for **2**. If we assume that the difference is due exclusively to intramolecular quenching, then the rate constant for this process would be ~2 × 10^8 s^{-1}. Perhaps a more accurate estimate can be obtained by subtracting the rates of decay observed for **2** from those measured for **3**. This approach assumes that all other modes of decay available to **3** proceed with the same rate constants as in the case of **2**.[44] This analysis in the 184 to 217 K range leads to log (A/s^{-1}) = 13.05 and E_a = 6.43 kcal/mol, corresponding to a rate constant for the interaction of 2.3 × 10^8 s^{-1} at 300 K. The efficient deactivation of triplet **3** could be expected to involve exciplex formation in much the same fashion as in several alkanone–arene systems reported by Wilson, Frye, and Halpern.[26] However, all attempts to detect this exciplex by direct detection, or using the dibromoanthracene sensitized fluorescence, as in Wilson and Halpern's method, were unsuccessful.

It is instructive to compare the quenching parameters for the triplet state of **3** (k_{ex} = 2 × 10^8 s^{-1}) with those for open-chain analogues. For example, γ-phenylbutyrophenone undergoes type II photoelimination with high efficiency (Φ = 0.49) and decays with a normal rate constant of 4 × 10^8 s^{-1}, compared to Φ = 0.33 and k = 1.4 × 10^8 s^{-1} for valerophenone.[45] Thus, the electrophilic oxygen preferentially abstracts hydrogen via a six-center transition state, as opposed to exciplex formation with the adjacent aromatic ring. In β-phenylpropiophenones (βPP)[13] the situation is reversed, with exciplex formation being favored by the shorter backbone link. It is interesting to note that despite the larger ring size involved in exciplex formation with **3**, our calculated A factor [log

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(34) Adamantanone, a similarly constrained cyclic ketone, is also quite stable: Sasaki, T.; Eguchi, S.; Mizutani, M. *Synth. Commun.* **1973**, *3*, 369.

(35) Weir, D.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *118*, 526.

(36) Salem and Rowland[37] have shown that spin–orbit coupling, a major intersystem crossing mechanism, is most important at short end-to-end distances. Recent work[38] on benzyl–acyl biradicals suggests that intersystem crossing "requires a nearly cyclic conformation with small end-to-end distance". Caldwell et al.[39] report that for *cis*-1-benzoyl-2-benzhydrylcyclohexane the biradical lifetime is not shorter than that for the unrestricted analogue derived from γ,γ-diphenylbutyrophenone; however, it is likely that while the cyclic ketone does keep the ends closer than in the open chain analogue, it also reduces the accessibility of the most favorable, fully eclipsed conformation.[40]

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(A/s^{-1}) is 12.5 or 13.05 depending on whether the uncorrected or corrected value is preferred] is considerably larger than that found for βPP (10.5).[13] Presumably, little molecular reorganization is required to orient the phenyl ring in **3** for complexation in contrast to the situation in βPP. While entropy terms clearly favor **3** over βPP, the situation is reversed in the case of the activation energies for decay (2.3 and 5.6–6.4 kcal/mol for βPP and **3**, respectively),[13] probably reflecting that the interaction with the electron-poor n-orbital in the carbonyl is restricted in the case of **3**.

The ratio of intersystem crossing yields $\Phi^3_{ISC}/\Phi^2_{ISC}$ of 0.13 (at −60 °C) leads to the expectation and observation of fluorescence from **3** in solution at 77 K (fluorescence and intersystem crossing are usually competitive processes in aliphatic carbonyls). The low value of Φ^3_{ISC} does, however, pose significant experimental problems in the study of triplet **3** (weak signals) and has limited the temperature range that we could examine.

Extrapolation of the triplet data (Table III) to 77 K leads to "expected" lifetimes which are much longer than the measured values (Table IV). Thus, carbonyl deactivation by the *syn*-phenyl ring in **3** does not seem to be an active decay path under these conditions; it would thus appear that at 77 K the role of the phenyl ring is reduced to providing some steric protection to the carbonyl triplet.

The behavior of the anti ketone, **2**, parallels the behavior of the exo systems studied by Amrein and Schaffner[4] in that energy transfer from the aryl groups is much faster than fluorescence.

Work is continuing in this and related areas in an effort to further our understanding of the importance of stereoelectronic and other factors that might be involved in these deactivation mechanisms.

Experimental Section

Ultraviolet absorption spectra were recorded on a Cary-Varian 219 or a Hewlett-Packard 8451 diode array spectrometer. Fluorescence and phosphorescence emission spectra as well as phosphorescence lifetimes were obtained on a Perkin-Elmer LS-5 spectrofluorometer equipped with a PE Model-3600 data station. Room temperature spectra were recorded with use of 10 mm path length quartz cells while spectra at 77 K were obtained inside a rectangular quartz dewar with 3 mm diameter quartz sample tubes.

Quantum yields of fluorescence were measured by the method of Parker and Rees[46] with norcamphor (Φ_F = 0.0033)[47] as a standard. All spectra were determined in HPLC-grade acetonitrile (Fisher). Optical densities of standard and unknowns were adjusted to within 1% at the excitation wavelength, and all solutions were purged with nitrogen prior to the measurements. Accuracy is believed to be better than ±10%. Fluorescence lifetimes were determined by time-correlated single-photon counting with a PRA instrument interfaced to a PDP-11/73 computer equipped with one and two exponential deconvolution programs as well as curve fitting and graphics programs.

Solutions of **1** (0.35 M), **2** (0.25 M), and **3** (0.25 M) in acetonitrile-d_3 were deaerated with dry nitrogen and irradiated at ~300 nm at ~30 °C for 47 h in a Rayonet reactor. Faint turbidity developed in **1** and **3**, but there was no substantial loss of starting materials as monitored by ^{1}H NMR spectroscopy.

Laser flash photolysis experiments were carried out with use of the pulses (308 nm, ≤80 mJ/pulse, ~4 ns) from a lumonics TE 860-2 excimer laser filled with a Xe–HCl–He mixture. Samples contained in 7 × 7 mm^2 rectangular quartz cells were deoxygenated by bubbling with dry nitrogen. A more detailed description of the laser system is given elsewhere.[48]

***anti*-11-Phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one.** To a solution of 2.00 g (7.5 mmol) of ketal **5** in 50 mL of absolute ethanol was added 5 teaspoons of freshly prepared W-4 Raney nickel.[49] The mixture was stirred for 40 min at 25 °C. The nickel was removed by filtration and washed with ethanol. The combined filtrates were evaporated to give 1.59 g of crude ketone that was contaminated with some alcoholic impurity which was removed by oxidation. The ketone was dissolved in 35 mL of cold ether and treated with a cold solution of 7.5 g of $Na_2Cr_2O_7 \cdot 2H_2O$ in 5.7 mL of H_2SO_4 and 30 mL of water. The reaction mixture was stirred at 0 °C for 1 h. The layers were separated and the aqueous layer was extracted with 50 mL of ether. The combined extracts were washed with aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated. The residue was purified by flash chromatography (silica gel) with $CHCl_3$ as eluent followed by crystallization from 65% aqueous ethanol. **2** (1.18 g, 66%) was obtained as white crystals, mp 99–100 °C (lit.[23] mp 96–100 °C).

The sample used for fluorescence measurements was purified by rechromatography on a silica gel column that was flushed with absolute ethanol followed by freshly purified $CHCl_3$ which contained 0.75% ethanol. After elution with $CHCl_3$ the ketone was crystallized twice from aqueous ethanol.

***anti*-11-Bromo-*syn*-11-phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (6).** A solution of 0.502 g (1.88 mmol) of **5** in 10 mL of 30% HBr in acetic acid was stirred at 25 °C for 1 h. The reaction mixture was diluted with 100 mL of ether followed by aqueous washing (2 × 100 mL) and once with 100 mL of 5% aqueous $NaHCO_3$. The dried ($MgSO_4$) extracts were partially evaporated and cooled to give 0.376 g (60%) of **6**: mp 143–145 °C; IR (KBr) 1740 cm^{-1} (C=O); NMR δ 7.2–7.6 (m), 4.0–2.2 (m), 2.2–1.6 (dd, J_{AB} = 10 Hz, CH_2). Anal. Calcd for $C_{17}H_{15}BrO$: C, 64.78; H, 4.80. Found: C, 64.54; H, 5.09.

***syn*-11-Phenylpentacyclo[5.4.0.0^{2,6}0^{3,10}0^{5,9}]undecan-8-one (3).** A solution of 6.80 g (0.22 mol) of **6** in 325 mL of absolute ethanol was stirred with 0.68 g of 10% palladium/charcoal under an atmosphere of hydrogen until TLC analysis indicated complete reaction (several hours). The reaction mixture was filtered followed by rotary evaporation. The crude product was flash chromatographed and crystallized from 65% aqueous ethanol and 85% aqueous methanol to yield 0.532 g (10%): mp 96–67 °C; IR (KBr) 1740 cm^{-1} (C=O); NMR δ 7.2 (s), 3.8–2.2 (m), 3.2 (t, J = 3 Hz), 2.2–1.4 (dd, J_{AB} = 11 Hz, CH_2). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.64; H, 7.09.

The sample used for fluorescence measurements was re-chromatographed as described above and then crystallized twice from cyclohexane.

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Registry No. **1**, 69649-19-0; **2**, 85507-41-1; **3**, 105087-87-4; **5** (Ar = Ph), 85507-47-7; **6**, 105018-78-8.

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