by the bond angles. Isotropic thermal parameters reveal that the atoms bonded to C_9 are relatively free to vibrate ($B \simeq 8\ \text{Å}^2$) and that C_1 and C_2 are rigid ($B \simeq 3.5\ \text{Å}^2$). This supports the proposal[1] that C_2 behaves like a bridgehead carbon atom in a rigid ring.

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Concerning the Phosphorescence of Phenyl Alkyl Ketones

Sir:

The spectroscopy[1–8] and photochemistry[8–15] of phenyl alkyl ketones are very interesting and have received much recent attention, primarily because the two lowest triplets of these compounds—one mostly n,π^* and one mostly π,π^*—lie very close together, their relative energy levels being quite substituent and solvent sensitive. Despite the fact that all workers acknowledge the energetic proximity of these two triplet levels, the possibility that they may attain thermal equilibrium before decaying has been almost totally ignored in published interpretations of the photobehavior of phenyl ketones.

In *nonpolar* media, the L_a π,π^* triplet of phenyl alkyl ketones presumably lies only a few hundred reciprocal centimeters above the lowest, n,π^* triplet.[3] Change to a polar medium[3,7,10] or the addition of electron-donating substituents[2,8] inverts the ordering. For ΔE of 250 cm^{-1} (700 cal), 1% of the triplets would exist in the upper state *at equilibrium*, even at 77°K. Such an equilibrium situation would not affect phosphorescence when the $^3n,\pi^*$ state is lower; but it would when the $^3\pi,\pi^*$ state is lower, because of the much faster emission rate of the $^3n,\pi^*$ state. We want to point out that some of our results as well as those of others are best interpreted as phosphorescence from an equilibrium mixture of both triplets.

Several authors have reported that in moderately polar solvents the overall phosphorescence decay of phenyl alkyl ketones is nonexponential, consisting of both a long-lived and a short-lived component.[1,3,7,10,14,16] These reports suggest that the short-lived component is the $^3n,\pi^*$ state, while the long-lived component is a state of mostly $^3\pi,\pi^*$ character. For such an interpretation to be correct, however, the two states could not be in equilibrium. But a nonequilibrium distribution would not be expected to occur unless internal conversion between the states were slower than phosphorescence, which seems highly improbable. Lim and coworkers have pointed out this problem and have offered a new interpretation.[17] They observe the same two-component phosphorescence from 1-indanone originally reported by Yang and Murov.[1] However, they find that 2,2-dimethyl-1-indanone, which possesses no protons α to the carbonyl, displays only short-lived emission and suggest that the long-lived emission from indanone arises from an excited enolate ion.

In agreement with previous reports, we find that all of a dozen various straight-chain phenyl alkyl ketones of the general formula $PhCOCH_2R$, as well as some ring-halogenated ketones, display both short- and long-lived phosphorescence in several solvents at 77°K.[18] The percentage of long-lived emission increases with the basicity of the solvent. However, both α,α-dimethylpropiophenone and α,α-dimethylvalerophenone display only short-lived emission through seven half-lives, even in a glass containing triethylamine. Their spectra resemble that of benzophenone closely, having classic n,π^* structure. The differences between the spectrum of valerophenone and that of its α-dimethyl derivative are very similar to those reported for the indanone system.[17] In particular, the slow emission seems to come from a state slightly *lower* in energy than the fast emitter. Table I contains those results of ours and others most pertinent to the problem.

We would make two points. First, we note that there is no significant polar solvent effect on the emission lifetime of benzophenone, whose lowest triplet is clearly n,π^*.[19] For the *p*-chloro ketone and for valerophenone, however, there is a substantial effect, such that the faster emitting component in ethanol is too slow to originate solely from an n,π^* state; such is also the case foi the *p*-fluoro ketone in isopentane. Other workers have also reported intermediate phosphorescence lifetimes for *p*-chlorophenyl ketones,[6,13] which we suggest are due to the following equilibrium

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Table I. Phosphorescence of Some Phenyl Ketones with n,π^* Lowest Triplets

Ketone	Solvent	E_T,[a] kcal	τ_{short}, msec	τ_{long}, msec[b]
PhCOPh	MC[c]	68.6	5.6	None
	EtOH	69.5	6.2	None
$PhCO(CH_2)_3CH_3$	2-MP[d]	74.5	6.4	(2) 27
	EtOH	74.3	34	(6) 260
	EPT[e]	74.4	27	(17) 74
$PhCOCMe_2(CH_2)_2CH_3$	EPT	72.5	5.5	None
$PhCOCMe_3$	MC	72.0	4.4	None
	EtOH	72.6	7.3	None
$PhCOCH_3$[f]	MC	73.5	4	None
	EtOH	74.0	8.0	(3) 200
1-Indanone[g,h]	3-MP[i]	75.1	1.5	None,[g] 130[h]
	EPA	75.8	2.2	(30) 200[h]
2,2-di-Me-1-indanone[g]	3-MP	74.0	1.7	None
	EPA	74.6	1.9	None
1-Tetralone[g]	3-MP	72.4	2.9	None
	EPA	72.9	3.8	None
p-F-$PhCO(CH_2)_3CH_3$	IP[j]	72.5	39	(19) 130
p-Cl-$PhCO(CH_2)_3CH_3$	IP	70.5	4.7	(7) 75
	EtOH	72.2	40	(50) 100

[a] 0–0 band. [b] Number in parentheses equals percentage of total emission (at 0–0 band). [c] Methylcyclohexane. [d] 2-Methylpentane. [e] 5:5:2 ether–isopentane–triethylamine. [f] Reference 3. [g] Reference 17. [h] Reference 1. [i] 3-Methylpentane. [j] Isopentane.

scheme, where $X_{n,\pi}$ is the fraction of triplets in the $^3n,\pi^*$ state at equilibrium.

$$\begin{tikzcd} & \underline{10\%\,{}^3n,\pi^*} \arrow[r, "\sim 200\ \text{sec}^{-1}"] \arrow[d, shift left] & \sim 80\%\ n,\pi^*\ \text{emission} \\ \Delta E \approx 350\ \text{cal} & \underline{90\%\,{}^3\pi,\pi^*} \arrow[u, shift left] \arrow[r, "\sim 5\ \text{sec}^{-1}"] & \sim 20\%\ \pi,\pi^*\ \text{emission} \end{tikzcd}$$

$$1/\tau = X_{n,\pi}k_{n,\pi} + (1 - X_{n,\pi})k_{\pi,\pi} \qquad (1)$$

$$\ln\left(\frac{1 - X_{n,\pi}}{X_{n,\pi}}\right) = \frac{\Delta E}{RT} \qquad (2)$$

Independent evidence for this assignment is provided (1) by the heavy-atom effect on the lowest energy S $\rightarrow$ T* absorption;[2] (2) by the n,π^* polarization of the highest energy (supposed 0–0) phosphorescence band;[6] and (3) by the overall n,π^*-like appearance of the phosphorescence spectrum.[2,6] We also note that Lamola has recently observed such an equilibrium mixture of n,π^* and π,π^* triplets in the phosphorescence of a compound containing two separate, nonconjugated chromophores with similar triplet excitation energies.[20]

If the shorter lived component from the halo ketones and from valerophenone in ethanol represents an equilibrium mixture of n,π^* and π,π^* triplets, we must ask then what the longer lived component can be, not only in these ketones but in all cases. We tend to agree with Lim[17] that the long-lived emission does not come directly from the π,π^* triplet. Not only is it awkward to postulate that some of the π,π^* triplets equilibrate with the n,π^* triplet while others do not, it is very difficult to rationalize the lower energy state affording the minor emission component. However, the lack of long-lived phosphorescence from the ketones with no enolizable α hydrogens does not in itself provide unequivocal evidence that the long-lived emission, where observed, involves an enolate ion. Dimethyl substitution at the α position lowers the triplet n $\rightarrow$ π^* transition energy by 1–2 kcal but does not affect λ_{max} for the $^1A \rightarrow {}^1L_a$ transition, so that the triplet $\pi \rightarrow \pi^*$ transition energy presumably remains constant at 75–76 kcal.[3] Moreover, our unpublished results with pyridyl ketones agree with those of Yang with trifluoromethylphenyl ketones:[12] neither produces any long-lived emission in hydrocarbon glasses. In both kinds of ketones, the $^3n,\pi^*$ state is stabilized relative to the $^3\pi,\pi^*$ state. Consequently, the amount of long-lived emission correlates better with the $^3n,\pi^*$–$^3\pi,\pi^*$ energy separation than it does with the enolizability of the α protons. The observation of a long-lived component, even when the $^3n,\pi^*$ state is lowest, then seems to be diagnostic of the proximity of a $^3\pi,\pi^*$ state, as originally suggested by Yang and Murov.[1]

In summary, a comparison of our results with those of others suggests that the shorter lived phosphorescence component from phenyl alkyl ketones arises from an equilibrium mixture of $^3n,\pi^*$ and $^3\pi,\pi^*$ states. The longer lived component may well involve nonequilibrium loss of an α proton because of its increased importance in basic solvents and because of the reported photoaldol condensation of 1-indanone in isopropyl alcohol.[21] However, its dependence on the $^3n,\pi^*$–$^3\pi,\pi^*$ energy separation, which suggests a $^3\pi,\pi^*$ precursor, is in direct conflict with the results of Lim's polarization measurements,[17] which suggest a $^3n,\pi^*$ precursor.

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Cyclopropane Assistance in Neopentyl Solvolysis[1]

Sir:

The effectiveness of neighboring group participation by cyclopropane in solvolytic reactions has been investigated recently by several groups.[2] In contrast to the

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