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Time-Resolved Diffuse Reflectance Studies of *β*-Phenyl Ketones in the Solid State: Conformational and Chiral Control of Triplet Lifetimes

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The triplet states of ketones having a *β*-aryl substituent, such as **2** and **3**, decay in solution by a charge transfer interaction between this aryl group and the excited carbonyl. In the solid state, this interaction also provides an efficient mode of deactivation for **3**, but not for **2**, reflecting the proximity between the *π*-ring system in **3**, but not in **2**, where the molecules crystallize (X-ray) in a stretched conformation. In the case of **3**, the triplet lifetime in the solid state is 420 ns for the pure *R* or *S* enantiomers, but 733 ns for the racemic crystals, showing an interesting case of chiral discrimination. Powder X-ray and solid state NMR data suggest that conformational and packing differences between the enantiomers and racemic crystals are responsible for differences in the efficiency of intramolecular deactivation.

Introduction

Triplet states of ketones, such as **2**, decay via a well-known intramolecular deactivation process involving the *β*-phenyl ring.[1−6] The process is thought to involve a charge transfer interaction between the carbonyl n,*π** triplet state and the *β*-aryl ring[7,8] and requires good overlap between the aromatic ring's *π* system and the carbonyl group.[6] Studies in solution have revealed that the triplet lifetimes observed are sensitive to conformational changes induced by the environment or by substituents attached to various parts of the molecule. Incorporating these ketones into hosts such as cyclodextrins and zeolites significantly lengthens the triplet lifetime by hindering the movement of the *β*-phenyl ring.[9−12] The addition of methyl groups on either the *β*-position or on the *β*-phenyl ring itself can dramatically affect the triplet lifetime, depending on the number and location of the substituents.[7] The effects of *β*-methyl substitution are attributed to restrictions in the rotation of the aryl ring away from the carbonyl which results in a more "locked" conformation and shorter triplet lifetime. In the latter case, reductions in the oxidation potential of the *β*-phenyl ring with aryl substituents results in similar reductions in triplet lifetimes.[7,8,13]

In solution, the effects of *β*-aryl substituents are well documented; however, only a limited amount of work has been done with *β*-aryl ketones in the solid state. In other photochemical systems, Scheffer *et al.* have reported extensive research on the influence of reaction media on the reactivity of ketones, especially in crystals.[14,15] Traditionally, the rationalization of reaction pathways has been carried out indirectly by analyzing X-ray data and product distributions to best understand photochemical mechanisms in the solid state. Monitoring directly the excited states controlling the photochemistry in the solid can be used to further complement our understanding of solid state photochemical mechanisms.

The transient behavior of lignin model compounds, also containing a *β*-aryl group, have been studied in the solid state, as well as on silica, zeolite, and cellulose supports.[13,16] However, the observations are complicated by cleavage of the starting materials upon laser excitation to form radicals and products which also can absorb light. Ketones, such as **2** and **3**, where cleavage of the starting material is not a major process, simplify the transient solid state photochemistry.

In this paper, we report that the effect of conformational changes on triplet lifetimes which were reported earlier in solution are even more prevalent in the solid state. By using diffuse reflectance laser flash photolysis techniques on solid samples of these ketones, we are able to demonstrate that conformational effects also play a significant role in the solid state. We also demonstrate that the triplet state of ketone **3** can distinguish packing differences in crystals of pure enantiomers and racemic mixtures. These results are then rationalized through the triplet lifetimes observed along with powder and single-crystal X-ray crystallography.

Experimental Section

Materials. Solvents used for synthesis and laser flash photolysis were obtained from BDH (Omnisolv, glass distilled) and were used without further purification.

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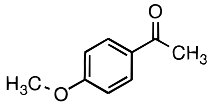
p-Methoxyacetophenone (**1**) was purchased from Aldrich and recrystallized once from ethanol. Ketones **2** and **3** were prepared following a literature method.[7] For **2** the spectroscopic properties are as reported earlier,[7] mp 95−97 °C. Anal. Found: C, 79.87; H, 6.74. Calcd for $C_{16}H_{16}O_2$ (**2**): C, 79.97; H, 6.71.

(*R*)- and (*S*)-3-phenyl butyric acid (Fluka) were used as starting materials to make the pure isomers **3R** and **3S** using the same method. The melting points of **3R** and **3S** were 53−54 °C while **3rac** was 86.5−87 °C. **3rac.** Anal. Found: C, 80.06; H, 7.04. **3S.** C, 80.40; H, 7.22. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. NMR data for **3** has been reported earlier.[7] The optical rotation ($[\alpha]^{20}$) measured with the sodium D line was +15.7° for **3R** and −14.7° for **3S**. Optical purity was verified by the lack of separation of the pure enantiomers on HPLC using a chiralcel OB column (J.T. Baker Inc.) and chiral shift reagent analysis using tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium (III) derivative (Aldrich) on ^1H NMR. The techniques mentioned above were able to readily resolve the two enantiomers making up **3rac**.



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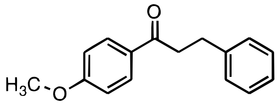

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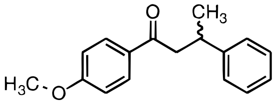

3

Laser Flash Photolysis. The samples contained in 3 × 7 mm^2 Suprasil quartz cuvettes were excited by pulses (308 nm; <30 mJ; ∼8 ns) from a Lumonics excimer laser. A Tektronix 2440 digitizer was used to capture the transient signals. The data were transferred via GPIB interface to a Macintosh IIci computer which controls the experiments and provides processing facilities through a home-developed program using LabVIEW-2.2 software from National Instruments. Further details on the time-resolved diffuse reflectance technique have been given elsewhere.[17]

The data analysis was based on the fraction of reflected light absorbed by the transient (reflectance change = $\Delta J/Jo$) where Jo is the reflectance intensity before excitation and ΔJ is the change in the reflectance after excitation. For moderate values of reflectance change, such as observed in the present work, this function is linear with concentration.[18]

NMR Spectra. The ^{13}C CP/MAS NMR data were collected on a Bruker ASX-200 NMR spectrometer equipped with a 7 mm MAS probe. The cross polarization technique was employed with suppression of first-order spinning side bands.[19] The ^1H $\pi/2$ pulse was 3.6 μs in duration, the contact time was 1 ms, and the relaxation delay was 4 s. The samples were spun at 5000 Hz. In all spectra, 128 transients were signal averaged. Each free induction decay was collected with 3K data points which were zero filled to 16K prior to Fourier transformation. The spectral window spanned 17774 Hz. No line broadening or resolution enhancement was applied to the data. The dipolar dephasing technique[20] was used to partially assign the spectra. The dephasing delay was 40 μs and yielded spectra consisting of only carbonyl, quaternary, and methyl carbon resonances. The chemical shifts were indirectly referenced to tetramethylsilane by external referencing to tetrakis(trimethylsilylsilane) at 3.7 ppm from TMS at 0 ppm and were in good agreement with previous solution ^{13}C NMR data reported above.[7] **3S** gave the following signals (δ, ppm): 24.8 (CH_3), 36.5 (CH), 46.5 (CH_2), 53.7 (CH_3), 110.8 (CH), 117.1 (CH), 126.8−131.2 (unresolved C and CH), 148.1 (C), 163.3 (C), and 196.2 (CO). **3rac** gave the following signals (δ, ppm): 25.4 (CH_3), 37.1 (CH), 44.7 (CH_2), 53.6 (CH_3), 109.4 (CH), 117.2 (CH), 126.0−131.4 (unresolved C and CH), 147.8 (C), 163.0 (C), and 198.4 (CO).

Crystallographic Data. The crystals of approximate dimensions 0.2 × 0.05 × 0.2 mm and 0.2 × 0.2 × 0.2 mm for ketones **2** and **3S**, respectively, were mounted on a glass capillary and diffraction measurements made on a Rigaku diffractometer with Mo Kα radiation. Other apparatus and data handling details are given elsewhere.[16] Both ketones **2** and **3S** corresponded to orthorhombic cells, the former having cell dimensions of $a = 10.340(13)$, $b = 31.00(4)$, and $c = 8.073(8)$ Å and the latter having dimensions $a = 8.0283(26)$, $b = 31.2398(143)$, $c = 5.6805(35)$ Å. Ketones **2** and **3S** had calculated densities of 1.233 and 1.186 g/cm^3, as well as formula weights of 240.30 and 254.33, respectively.

Powder X-ray spectra were collected using a Philips PW1827/91 X'Pert System powder X-ray diffractometer. PC-ITO (Visser, 1969)[21] software was used to index the powder X-ray diffraction patterns for **3rac**. **3S** was also calculated in the same way and compared to the values obtained from the single-crystal X-ray data. The unit cell dimensions calculated for **3rac** were 16.6 × 12.9 × 14.1 Å; $\alpha = \gamma = 90°$; $\beta = 103°$. All the lines obtained in the powder X-ray pattern were accounted for. Similarly, the unit cell for **3S** was calculated as 8.0 × 31.3 × 5.7 Å, $\alpha = \beta = \gamma = 90°$ with all lines accounted for, and is in good agreement with the single-crystal X-ray data given above.

Luminescence Spectroscopy. These measurements were carried out using the third harmonic (355 nm) from a Continuum PY-61 picosecond YAG laser for excitation and a Hamamatsu fluorescence measurement system based on a Model C4334 Streakscope.

Steady State Irradiations. Solid samples were contained in small ∼10 mL Suprasil quartz tubes which were continually rotated in the irradiation chamber to ensure homogeneous light exposure. The samples were irradiated in a reactor equipped with nine RPR-300 nm lamps. The temperature of the irradiation chamber was in the 30−35 °C range. GC−MS analysis was carried out with a Fisons Instruments GC 8000 series with MD800 mass selective detector.

Results

The transient behavior of the ketones examined in this study have been investigated in solution and have already been reported.[6,7] Transient phenomena in β-aryl ketones are generally dominated by a strong triplet absorption around 400 nm (Figure 1) having a relatively fast decay due to an efficient intramolecular deactivation mechanism. The triplet absorption spectra obtained in the solid state from ketones **2** and **3** were virtually identical to those obtained in homogeneous solution. Both spectra had maxima at around 400 nm and can be readily assigned to the triplet state.[6] Figure 1 shows a typical solid state triplet absorption spectrum of ketone **3rac** collected after 308 nm laser irradiation. Ketones **2** and **3** gave similar triplet spectra in the solid state, and the addition of oxygen had no effect on their triplet spectra or lifetimes. In solution, the triplets of these ketones are efficiently quenched by oxygen. This indicates that the penetration of oxygen through the crystal lattice is very inefficient. The lack of oxygen effect on solid state triplet lifetimes has been reported elsewhere.[13]

Comparisons of the triplet lifetimes in solution and the solid state for the ketones studied are shown in Table 1. The lifetimes are much longer in the solid state for all

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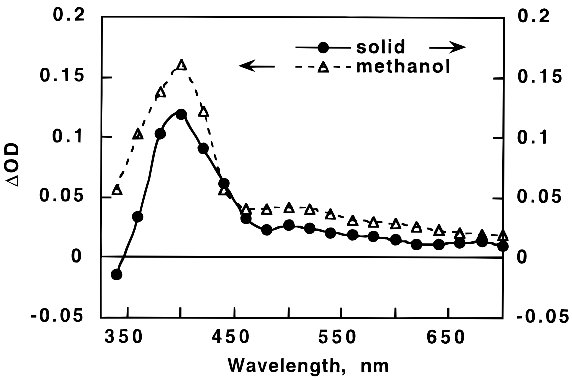

Figure 1. Transient absorption spectra of **3rac** in methanol (Δ) and in the solid state (●) monitored 16 and 22 ns, respectively, after 308 nm laser excitation. Expressed as ΔOD in solution and as Δ*J*/*J* in the solid state.

Table 1. Lifetimes (ns) in Methanol Solution and in the Solid State

	lifetimes (ns)[a]	
	solution[b]	solid
1	≥2000	1930/10900[c]
2	200	8000
3rac	95	733
3R	95	415
3S	95	425

[a] ± 10%. [b] Under a nitrogen atmosphere. [c] Biexponential decay, see text.

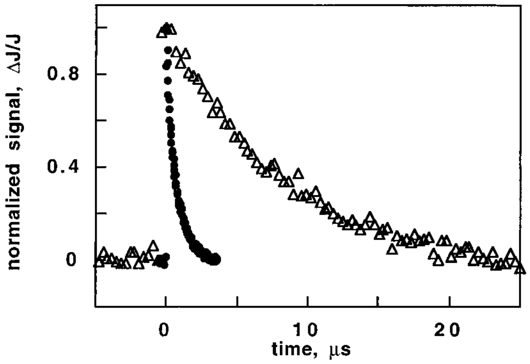

Figure 2. Transient absorption decays of **2** (Δ) and **3rac** (●) in the solid state monitored at 400 nm after 308 nm laser excitation.

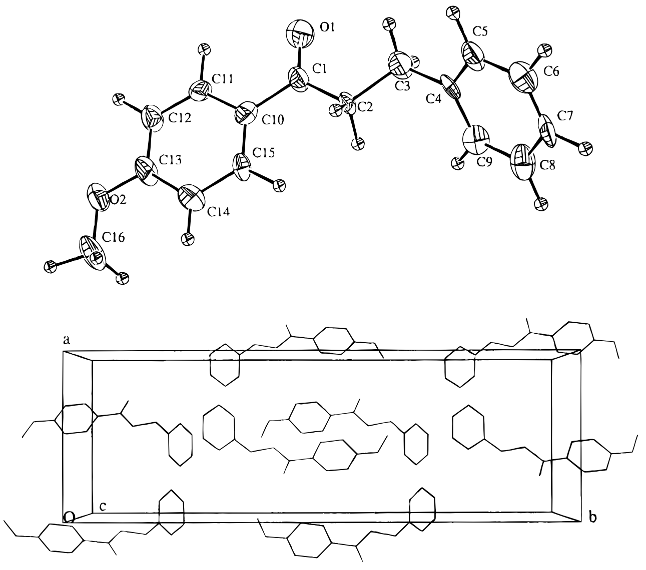

Figure 3. X-ray crystal structure of ketone **2** (top) and the arrangement of the molecules in the unit cell (bottom).

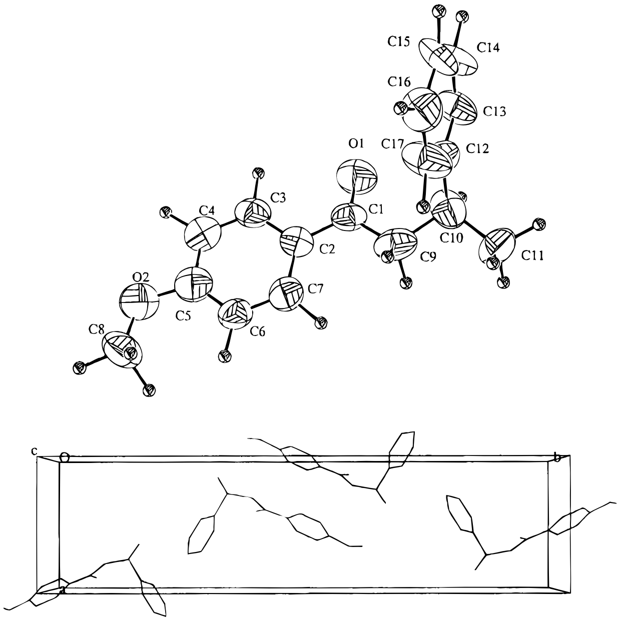

Figure 4. X-ray crystal structure of ketone **3S** (top) and the arrangement of the molecules in the unit cell (bottom).

the ketones, reflecting, as expected, the highly restricted mobility of the deactivating β-phenyl ring in the solid. However, ketone **3** shows only a modest increase in lifetime in the solid compared to solution. A comparison of the triplet decay traces of ketones **2** and **3rac** monitored at 400 nm after 308 nm laser irradiation is shown in Figure 2. In solution, it is the β-phenyl ring which performs the deactivation of the carbonyl triplet. However, in the case of **2** in the solid state this may not be the case. Single-crystal X-ray crystallography was used to determine the orientation of ketones **2** and **3** in the solid state. Figures 3 and 4 show the crystal structures and unit cell arrangements for these two ketones. Both samples crystallized into orthorhombic unit cells having similar dimensions. Ketone **2** had unit cell dimensions of $a = 10.340(13)$, $b = 31.00(4)$, and $c = 8.073(8)$ Å and a density of 1.233 g/cm^3; **3S** had dimensions of $a = 8.0283$ (26), $b = 31.2398(143)$, and $c = 5.6805(35)$ Å and a density of 1.186 g/cm^3. Despite their similar chemical properties, a distinct difference is observed in the proximity of the β-phenyl ring to the carbonyl group. Ketone **3S** has the deactivating ring placed much closer to the carbonyl in the solid state, clearly making β-phenyl quenching a primary mechanism of triplet deactivation for this ketone. However, in the X-ray structure of ketone **2,** the β-phenyl ring is much farther away, making an intramolecular deactivation pathway highly improbable. The relative orientation of the aromatic benzoyl rings is illustrated in Figure 5. These are clearly too far for excimer formation mechanisms of the type that have been shown to be responsible for the decay in other systems.[16] The molecules are probably close enough for energy migration to occur, presumably leading to deactivation via defects or traps. The triplet deactivation processes for crystalline **2** and **3** are highly efficient as GC−MS analysis of air-equilibrated **2** and **3rac** crystals irradiated at 300 nm for more than 100 h revealed no detectable photochemical products or depletion of starting material.

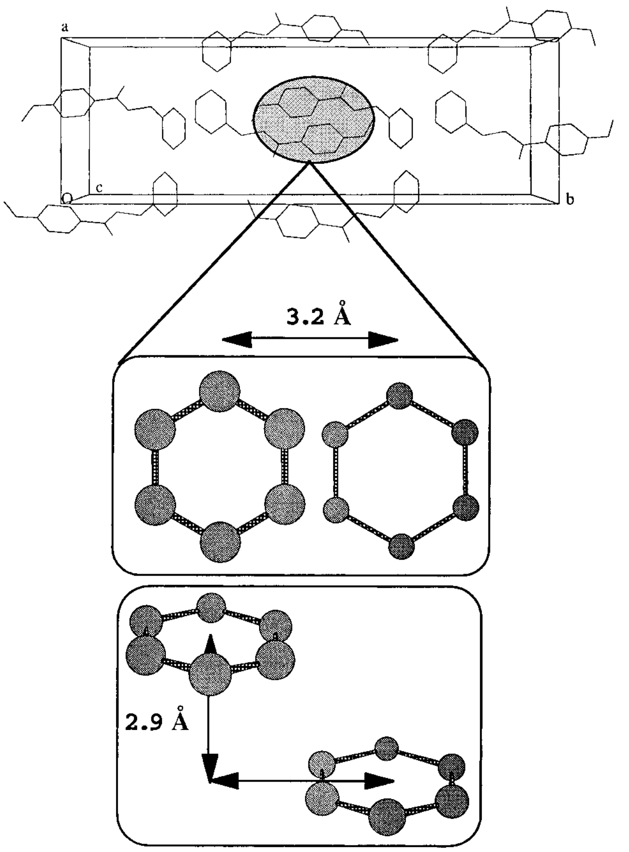

Figure 5. Unit cell for **2** and relative positioning of the aromatic ketone groups.

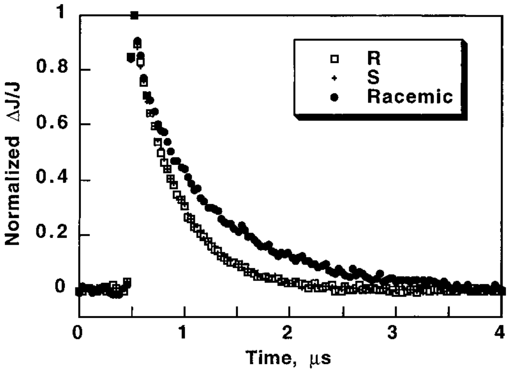

Figure 6. Transient absorption decay traces for **3rac**, **3R**, and **3S** in the solid state monitored at 400 nm after 308 nm laser excitation.

Of particular interest is the difference between the racemic crystal triplet lifetime and the pure enantiomers of **3**. We were surprised by a triplet lifetime nearly twice as long for the racemic crystals compared to that of the pure enantiomers, as seen in Table 1. Figure 6 shows the actual triplet decay traces of **3rac** compared to that of the pure enantiomers (**3**) monitored at 400 nm after 308 nm laser irradiation. In contrast, **3S** and **3R** give the same lifetime with superimposable decay traces. A number of attempts at growing crystals of **3rac** suitable for X-ray over a period of 2 years were unsuccessful. Several methods, including supersaturation, slow evaporation, and nucleation, were attempted in various solvents and solvent mixtures. In order to gain some insight into the structure of the racemic crystals, it was necessary to use powder X-ray and solid state NMR techniques to describe the differences in the crystal structures.

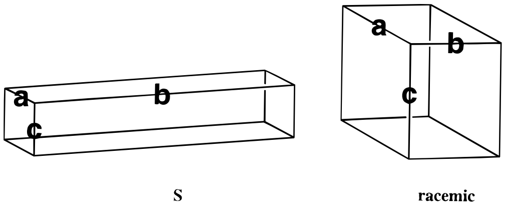

Figure 7. Unit cell dimensions of **3S** (left) and **3rac** (right) obtained from powder X-ray diffraction patterns using the PC-ITO program.[21]

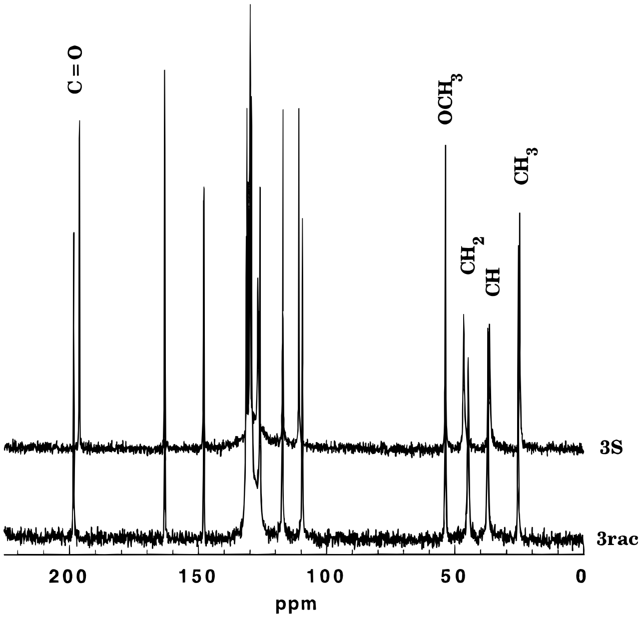

Figure 8. Solid state ^{13}C NMR spectra of **3S** and **3rac**. Selected carbon resonances are labeled.

Figure 7 shows the unit cell dimensions obtained from the powder X-ray diffraction pattern of **3S** and **3rac**. Unit cell dimensions were calculated using PC-ITO[21] software and an orthorhombic unit cell with dimensions 8.0 × 31.3 x 5.7 Å for the pure enantiomer (**3S**) giving a volume of 1400 A^3 and density of ca. 1.18 g/cm^3; **3rac** was calculated to have a *P*2 unit cell with dimensions 16.6 × 12.9 × 14.1 Å^3 ($\alpha = 90.0°$; $\beta = 103.4°$; $\gamma = 90.0°$) giving a volume of 2943 Å^3 and corresponding density of 1.16 g/cm^3. Verification of the calculations used in determining the unit cell dimensions of **3rac** was possible by analyzing the single-crystal X-ray diffraction data obtained from **3S** which correlated with the dimensions calculated by the PC-ITO software.

To further elucidate the structural differences between the racemic and pure enantiomer crystals, solid state ^{13}C NMR spectra of the two samples were recorded (Figure 8). Many of the chemical shifts for the **3rac** carbons are shifted downfield compared to **3S**, indicating a significant difference in the surrounding environment for these carbons. In particular, the carbonyl resonance for **3rac** shows a downfield shift of more than 2 ppm compared to **3S**.

To eliminate the possibility of impurities in the racemic crystals which may have caused the differences in lifetimes, a "synthetic" racemic was recrystallized from a mixture of equal portions of **3R** and **3S**. The newly made racemic crystals had the same properties as the "authentic" racemic including its triplet decay kinetics

Table 2. Luminescence Data for Various Ketones in the Solid State

	fluorescence[a]			
ketone	λ_{max}	τ [b]	notes	phosphorescence, τ
1	450	0.30/1.9	weak	~1600
2	440	0.54/1.8	shift[c]	~1800
3rac	440	0.22/1.8	shift[c]	~560
3S	424	0.23/1.4	weak	~390

[a] λ_{max} in nm and τ in ns. [b] Typically the short lifetime accounts for ~80% of the decay. [c] A pronounced shift to longer wavelengths with time is observed.

in the solid state. In contrast, a mechanical mixture of **3R** and **3S** showed typical pure enantiomer lifetimes, as expected.

The results of luminescence studies following 355 nm picosecond laser excitation have been summarized in Table 2. Phosphorescence was always extremely weak, and the emission may incorporate delayed fluorescence. While any detailed analysis would be highly speculative, it is clear that the values for **3S** and **3rac** are of the same magnitude and show the same differences as observed in the time-resolved diffuse reflectance work. Typical fluorescence lifetimes were around 300 ps with a longer (minor) component which may reflect the presence of traps or distinct surface sites.

Discussion

β-Aryl ketones have been used as mobility probes in heterogeneous systems, such as cyclodextrins and zeolites, because of the triplet lifetime's inherent sensitivity to mobility restrictions in confined spaces.[22] To effectively quench the carbonyl triplet state, a charge transfer interaction with the β-aryl ring is necessary. Confining the movement of the deactivating ring will result in longer triplet lifetimes in β-phenyl-substituted ketones. Changing substituents on the molecule will also act in a similar way by affecting the mobility of the β-aryl ring to either accelerate or slow down the decay, depending on the substitution pattern.[7]

In the case of **2**, the triplet decay in solution is quite long compared to other β-phenyl ketones, reflecting the presence of a low-lying π,π^* state due to the 4-methoxy substituent.[6] Deactivation occurs from a thermally populated n,π^* triplet state. The lifetime enhancement in **2** is even more pronounced in the solid state (see Table 1), where the triplet lifetime for **2** is extended by over an order of magnitude. Figure 2 shows the dramatic difference in triplet lifetimes observed. In solution, this is rationalized by the lack of steric confinements, such as methyl groups, which result in a facilitated rotation of the β-aryl ring away from the carbonyl.[7] In the solid state, **2** and **3S** both crystallize with orthorhombic unit cells with similar dimensions and densities. However, the crystal structure of **2**, shown in Figure 3, reveals a relatively flat stretched conformation with the β-aryl ring placed far away from the carbonyl, resulting in little or no intramolecular deactivation. In contrast, ketone **3S** (Figure 4) has a crystal structure which places the β-aryl ring much closer to the carbonyl group, thus resulting in a solid state triplet lifetime which is only about 4−6 times longer than in solution and more than an order of magnitude shorter than **2** in the solid state. The close and favorable position of the β-phenyl ring with respect to the carbonyl group facilitates the charge transfer interactions required for the deactivation of the triplet state.

In the case of **2**, the β-aryl ring is quite far from the carbonyl, and triplet deactivation must occur by an alternative mechanism. A comparison of the triplet decay kinetics of *p*-methoxyacetophenone (**1**) with **2** reveals triplet lifetimes of similar magnitude in the solid state (Table 1). This leads us to believe that triplet **2** may not require an interaction of the β-aryl ring to facilitate deactivation, although we note that the decay for **1** is best fitted by a biexponential decay with first-order components of approximately 2 and 11 μs. The crystal packing arrangement of the molecules in the unit cell of **2** may provide an alternative deactivation pathway. Of particular interest are the two center molecules in the unit cell shown in Figure 5. Their *p*-methoxybenzoyl moieties are aligned parallel to one another but displaced. While in other crystalline systems we have observed excimer-like deactivation mechanisms, including emission,[16] such a mode of decay appears unlikely here, since a "sandwich-like" arrangement is usually required for excimer-mediated deactivation. No excimer-like emission is observed, and the relevant moieties (see Figure 5) are too shifted for these interactions to occur. Most likely, the crystal packing provides a channel for energy migration to traps or surface sites from where deactivation takes place. Energy transfer is not expected to have the stringent orientation restrictions required for excimer formation. In the case of **1**, the longer triplet lifetime may represent deactivation through an energy migration to traps which is similar to **2**, while the shorter decay may represent an even more efficient unidentified deactivation process.

Differences in crystal packing can be inferred from the triplet decays of the racemic compound (**3rac**) and the pure enantiomers (**3R**, **3S**). We had suspected a difference in crystal packing judging from their respective melting points. The racemic form melts at 87 °C while the pure enantiomers melt at 53 °C. A more stable packing arrangement in the racemic form with greater intermolecular forces would be the cause of the elevated melting point and represents a more stable crystal lattice. Scheffer *et al.*[23] have observed different bimolecular reactivity in the solid state between dimorphs, which are defined as organic crystals of the same compound which pack in different symmetry relationships. We believe a similar phenomenon is occurring with the racemic and pure enantiomer crystals. Racemic mixtures in solution have been known to either crystallize and form a non-chiral racemic compound or undergo spontaneous resolution forming a mixture of chiral crystals. We believe that the former condition is occurring with **3rac**, thus resulting in a different crystal structure compared to the pure enantiomers. The analysis of a solid state ^{13}C NMR spectra (Figure 8) indicates slight differences in the peak positions of some of the carbons. In particular, the carbonyl group in the racemic crystal is shifted downfield almost 2 ppm when compared to the pure enantiomer crystals. This would indicate a substantial difference in crystal packing that leads to the chiral discrimination for the different triplet lifetimes of **3rac** and **3S**/**3R**.

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Structural information of **3S** was obtained from single crystal X-ray diffraction analysis of relatively easily made X-ray suitable single crystals of the pure enantiomer. A crystal large enough for single-crystal X-ray analysis could not be grown in the case of **3rac** even after numerous attempts. Very small crystalline needles were the only result. However, the unit cell dimensions of **3rac** were calculated from its powder X-ray diffraction pattern using PC-ITO software developed by Visser.[21] Figure 6 shows a scale representation of the unit cells of **3rac** and **3S**. The most obvious difference is the shapes of the unit cells and their respective volumes. The **3S** unit cell is long and rectangular, nearly twice as long as the almost cubical unit cell of **3rac**. The unit cell of **3S** has four molecules per cell, giving a density of 1.186 g/cm^3 and volume of 1400 Å^3. On the basis of density, there are eight molecules in the unit cell of **3rac**, giving a density of ca. 1.16 g/cm^3 and volume of 2900 Å^3. Although no conclusion can be made about the orientation of the molecules in the racemic crystal, the indirect evidence based on triplet lifetimes points toward a significant difference in crystal packing between the racemic and pure enantiomeric forms. This results in chiral discrimination in the decay kinetics of the ketones in the solid state. These changes in crystal packing must alter the position of the β-aryl ring in relation to the carbonyl in the solid state. Slightly closer packing in the racemic crystals may push the β-phenyl ring slightly away from the carbonyl, thus accounting for the longer triplet lifetime observed. This interpretation, while reasonable, must remain speculative, as there are no single-crystal structural studies of **3rac** to compare with those for **3S**.

Conclusion

We have successfully measured the triplet lifetimes of several β-aryl ketones in the solid state using laser flash diffuse reflectance photolysis techniques. Triplet absorption spectra show little cleavage of these ketones in the solid state upon laser excitation. The triplet lifetimes in the solid state are determined by the position of the β-phenyl ring in relation to the carbonyl. We have shown that ketones having methyl substitution in the β-position will crystallize with the deactivating ring closer to the carbonyl and result in faster decay kinetics when compared to unsubstituted ketones. Small packing differences in the unit cells will also be manifested in a change in triplet lifetime as seen from comparison of racemic to enantiomerically pure crystals.

In the past, β-aryl ketones have proven to be excellent mobility probes in heterogeneous solution. Our research indicates that ketone **3** would be an excellent mobility probe in solid state systems as well. Small changes in the position of the deactivating β-phenyl ring results in measurable changes in triplet lifetime.

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