# Strongly Entangled Triplet Acyl–Alkyl Radical Pairs in Crystals of Photostable Diphenylmethyl Adamantyl Ketones

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ABSTRACT: Radical	pairs generated in	crystalline solids by bond cleavage		

reactions of triplet ketones offer the unique opportunity to explore a frontier of spin dynamics where rigid radicals are highly entangled as the result of short interradical distances, large singlet—triplet energy gaps ( $\Delta E_{ST}$ ), and limited spin—lattice relaxation mechanisms. Here we report the pulsed laser generation and detection of strongly entangled triplet acyl—alkyl radical pairs generated in nanocrystalline suspensions of 1,1-diphenylmethyl 2-ketones with various 3-admantyl substituents. The sought-after triplet acyl—alkyl radical pairs could be studied for the first time in the solid state by taking advantage of the efficient triplet excited state  $\alpha$ -cleavage reactions of 1,1-diphenylmethyl ketones and the slow rate of CO loss from the acyl radicals, which would have to generate highly unstable phenyl and primary alkyl radicals or relatively unstable secondary and tertiary alkyl radicals. With the loss of CO prevented, the lifetime of the triplet acyl—alkyl radical pair intermediates is



determined by intersystem crossing to the singlet radical pair state, which is followed by immediate bond formation to the ground state starting ketone. Experimental results revealed biexponential kinetics with long-lived components that account for ca. 87-92% of the transient population and lifetimes that extend to the range of  $53-63 \mu s$ , the longest reported so far for this type of radical pair. Structural information inferred from the starting ketone will make it possible to analyze the affects of proximity and orientation of the singly occupied orbitals and potentially help set a path for the use of triplet radical pairs as qubits in quantum information technologies.

## INTRODUCTION

Reactions in crystals provide unique opportunities to explore chemical kinetics and spin dynamics under conditions that are not possible in any other media.<sup>1-10</sup> For example, using crystalline tetraarylacetones  $(1, R = CHAr_2; Scheme 1)$ , we have shown that pulsed laser excitation of nanocrystals suspended in water<sup>11</sup> makes it possible to detect triplet radical pairs <sup>3</sup>RP-2 formed by the loss of CO and to follow their subsequent decay to the corresponding photoproduct 2 (R = CHAr<sub>2</sub>).<sup>12</sup> The reaction starts by electronic excitation (step 1) and is followed by intersystem crossing (step 2) to the triplet excited state (<sup>3</sup>1<sup>\*</sup>), which goes on to cleave an  $\alpha$ -bond (step 3) to form a strongly correlated triplet acyl-alkyl radical pair  $({}^{3}\mathbf{RP-1})$ . When R = CHAr<sub>2</sub>, there is a rapid spin-conserving loss of CO to form the relatively long lived triplet alkyl-alkyl radical pair  ${}^{3}$ RP-2 (step 4), which goes on to the product 2 (step 7) through the singlet radical pair <sup>1</sup>RP-2 via a ratelimiting intersystem crossing step (step 6) shown to occur with time constants between 40 and 90  $\mu$ s depending on Ar.<sup>13,14</sup>

These rather long lifetimes are a strong indication that short inter-radical distances enforced by molecular crystals and the ensuing large singlet-triplet energy gaps ( $\Delta E_{ST}$ ) create an entangled spin system with limited intersystem crossing mechanisms.<sup>15-18</sup> As indicated in Figure 1, large  $\Delta E_{ST}$  values render an intersystem crossing mechanism based on hyperfine electron-nuclear interactions ineffective. Under these conditions, spin-orbit coupling is likely to operate even if the geometry of the singly occupied orbitals is not ideal and the closed-shell electronic states are likely to be much higher in energy in a nonpolar medium with a very low dielectric constant. Furthermore, short inter-radical distances and high radical asymmetry may lead to large zero-field splitting (ZFS) parameters such that equilibration between the spaced triplet sublevels  $(T_x, T_y)$  and  $T_z$  may be less likely. On the basis of this analysis we expected a triplet acyl-alkyl radical pair (<sup>3</sup>**RP**-1) to have significantly longer lifetimes in the solid state than in solution. An appealing feature of our hypothesis is that longlived and well-characterized spin states are promising platforms for quantum information science (QIS). In fact, molecular triplets formed by thermal activation or photoinduced charge transfer mechanisms have shown promise as spin qubit pairs (SOPs).<sup>19-23</sup> In contrast, strongly interacting transient qubits

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## Scheme 1



Nuclear Distance

**Figure 1.** Energetics of an  $\alpha$ -cleavage reaction in a triplet excited state crystalline ketone leading to the formation of the triplet acyl–alkyl radical pair <sup>3</sup>**RP-1** that is forced to remain within close to bond-distance proximity. The high rigidity and short inter-radical distance lead to a large ST energy gap and large zero-field splitting (ZFS) that energetically separate the  $T_{xy}$   $T_{yy}$  and  $T_z$  triplet sublevels, all of which inhibit the mechanisms for intersystem crossing.

resulting from photoinduced  $\sigma$  bond cleavage reactions constitute an alternative platform that has never been explored. With that in mind, useful photochemically responsive QIS materials should be able to (1) generate strongly entangled and spin-polarized triplet radical pairs upon the action of a short laser pulse,  $^{24}$  (2) favor conditions where the triplet radical pairs live sufficiently long for logic gate manipulation and readout using microwaves and/or optical methods, and (3) utilize a molecular unit that is reusable by virtue of the radical pair re-forming the starting material so that the corresponding qubits may be available multiple times upon demand. In this paper we explore a strategy based on the selection of the R group in Scheme 1 to prevent the formation of <sup>3</sup>**RP-2** in order to avoid product formation and in the process explore the lifetime of the triplet acyl-alkyl radical pairs <sup>3</sup>RP-1. It is known that strongly interacting triplet acyl-alkyl spin systems measured in short-chain biradicals have lifetimes that are much shorter than those of analogous dialkyl spin systems. A

significant difference in the g factors between the alkyl and acyl radical partners and greater spin-orbit coupling (SOC) in the carbonyl-containing  ${}^{3}$ **RP-1** provide intersystem crossing features that are not available to  ${}^{3}$ **RP-2**. In addition, a critical difference in the solid state in comparison to solution comes from the short electron-electron distances and high rigidity of crystals, which also limit potential spin-lattice relaxation mechanisms.

To prevent the chemical reaction and explore the lifetimes of acyl–alkyl radical pairs, we selected the diphenylmethyl adamantyl ketones in Scheme 1. A diphenylmethyl substituent was chosen both to facilitate a fast and efficient  $\alpha$ -cleavage reaction and to take advantage of the diphenylmethyl radical as a spectroscopic handle in pump–probe experiments carried out at 266 nm with the fourth harmonic of a nanosecond Nd:YAG laser. We selected adamantane as a building block in ketones **1b**–**d** to impart crystallinity and for the acyl radical generated upon light excitation to have a primary (**1b**), secondary (**1c**), or tertiary (**1d**) carbon at the  $\alpha$  position.<sup>25</sup> Acyl radicals with similar substituents in solution are known to lose CO with relatively long time constants of ca. 5 ms and 70 and 1.9  $\mu$ s (Table 1).<sup>26,27</sup> The tertiary radical that would be

## Table 1. Crystalline Ketones That Generate Transient Acyl–Alkyl Radical Pairs

ketone	R	mp (°C)	lifetime (µs) MeCN/ solid <sup>a</sup>	$ au_{-CO} \ (\mu s)^c$
1a	Ph	66.5-67.9	1.3/0.6, 1.5 (97) <sup>b</sup>	$\sim 10^{13} d$
1b	1-Adam	102.3-103.2	1.2/2.3, 53 (92) <sup>b</sup>	$\sim 5000^{d}$
1c	2-Adam	89.4-89.7	1.2/3.5, 61 (87) <sup>b</sup>	70
1d	3-Adam	104.4-105	$1.2/1.8, 63 (87)^{b}$	1.9

<sup>*a*</sup>Measurements in solids were carried out in aqueous nanocrystalline suspensions. <sup>*b*</sup>Percentage of radical decay accounted for by the long-lived component. <sup>*c*</sup>Decarbonylation rates for analogous free acyl radicals that generate phenyl, primary, secondary, and tertiary alkyl radicals.<sup>26,27</sup> <sup>*d*</sup>Measurements made in the gas phase.

generated by decarbonylation of 1d would be at the bridgehead position of the adamantyl group and therefore would be less stable than typical tertiary alkyl radicals.<sup>28</sup> Ketone 1a is expected to generate a benzoyl radical with a completely different electronic structure that is essentially stable toward the loss of CO, with an extrapolated time constant of ca. 0.32 years at 298 K.<sup>27</sup> While the rate of reaction from <sup>3</sup>RP-1 to <sup>3</sup>RP-2 by the loss of CO is likely to be different in crystals, in the absence of product formation we should be able to determine the intersystem crossing kinetics of the spinentangled <sup>3</sup>RP-1.

# RESULTS AND DISCUSSION

The synthesis of each ketone began with the reaction of commercially available diphenylmethane with *n*-butyllithium in tetrahydrofuran at 0 °C to form the corresponding lithium carbanion.<sup>29</sup> The appropriate acid chloride was added dropwise after stirring for 30 min. Acid chlorides were obtained by treatment of the corresponding acetic acid derivative with oxalyl chloride.<sup>30</sup> All four ketones were obtained in isolated chemical yields varying between 16% and 60% and were characterized by conventional spectroscopic methods (Supporting Information). Colorless crystals of 1a-d were obtained by slow evaporation from ethanol, and melting points were shown to vary from ca. 66.5 °C in the case of 1a up

to 104.4  $^{\circ}$ C in the case of 1d, which makes them suitable for solid-state spectroscopic measurements at ambient temperature.

A single crystal of 1d obtained from the ethanol recrystallization was analyzed by X-ray diffraction and the structure was solved in the monoclinic space group  $P2_1/c$  with two molecules with very nearly identical conformations in the asymmetric unit. The structure of one the two molecules in the crystal shown in Figure 2 has normal bond lengths and bond



**Figure 2.** (top left) Molecular structure of **1d** determined by a singlecrystal X-ray diffractions analysis, and (top right) line formula representation of the triplet acyl–alkyl biradical highlighting the close proximity between the unpaired electrons. (bottom) Space-filling model of the packing structure of ketone **1d** showing that significant separation and rehybridization of the two radical centers are unlikely.

angles with a conformation characterized by having one of the C–C bonds of the adamantane group nearly eclipsed with the carbonyl group, as indicated by a dihedral angle of  $1.56^{\circ}$ , while the  $\alpha$ -C–H bond is oriented almost antiperiplanar to the C== O group, with a dihedral angle of  $-171.51^{\circ}$ . As indicated in the figure, the  $\alpha$ -cleavage reaction is expected to occur at the weakest C–C bond, between the carbonyl carbon and the diphenylmethyl group carbon, which in the ground state has a normal bond length of 1.54 Å. It is worth pointing out that the dihedral angle between the plane of one of the aromatic rings and the cleaving C–C bond vector is close to orthogonal ( $D = 105.7^{\circ}$ ), which is necessary for the alkyl radical to experience benzylic stabilization.

Nanocrystalline suspensions of each ketone were prepared by dropwise addition of acetonitrile stock solutions into vortexing Millipore water containing cetrimonium bromide (CTAB) surfactant at ca. 4% of the critical micelle concentration.<sup>31</sup> Slightly turbid suspensions obtained in this manner were analyzed by dynamic light scattering, which revealed particle size distributions centered around 100–300 nm for each derivative, as indicated in the Supporting Information. Powder X-ray diffraction (PXRD) of each ketone measured with bulk solids as well as centrifuged nanocrystalline suspensions confirmed the same crystal polymorph. The corresponding PXRD patterns for 1d are shown in Figure 3 as representative examples, and the data for the other derivatives can be found in the Supporting Information.



**Figure 3.** Powder X-ray diffractogram of 1-((3R,5R,7R)-adamantan-1-yl)-2,2-diphenylethan-1-one (1d) in the bulk solid (bottom) and in nanocrystalline suspensions (middle) and the simulated pattern from the single crystal X-ray structure (top).

The strict solid-state photostability of crystalline ketones 1a-d was confirmed by extended exposure (up to 24 h) to UV light from a 500 W Hanovia medium-pressure mercury lamp, under conditions where complex reaction mixtures were obtained in solution. Interestingly,  $\alpha$ -adamantyl ketone 1b displayed no formation of Norrish-Yang cyclization products in the solid state, despite the presence of abstractable adamantane  $\gamma$ -hydrogen atoms,<sup>32</sup> highlighting a significant kinetic preference for the  $\alpha$ -cleavage reaction. Pump-probe experiments in solution and in nanocrystalline suspension were conducted with a single-pass flow system. Solution samples were sparged with argon or nitrogen gas for 1 h in order to remove dissolved oxygen. In the case of the nanocrystalline suspensions, DLS data were used to verify that suspensions remained stable for the duration of the pump-probe laser experiments. As shown in Figure 4 for ketone 1c, and as indicated in Table 1 for all four ketone samples, both solution and nanocrystalline suspensions produced a transient with a  $\lambda_{\rm max}$  value in the range of 320–340 nm that is consistent with the expected diphenylmethyl radical. The spectrum obtained with nanocrystalline suspensions (Figure 4, bottom) showed a substantially reduced intensity below 320 nm as a result of a large increase in light scattering and decreased transmittance at the shorter wavelength region.

Similar solution transients were observed for all four ketones, and decay measurements at 330 nm were shown to occur with a time constant  $\tau = 1.2-1.3 \ \mu s$  that is assigned to free radicals formed by rapid separation of the original radical pair followed by subsequent recombination. Analogous kinetic measurements carried out with nanocrystalline suspensions at  $\lambda_{\rm max} \approx 330$  nm could be fit using a double-exponential function with a small (3-13%) population of a short-lived component and a larger contribution (97-87%) from longer-lived triplet radical pairs. Notably, the intersystem crossing kinetics from the electronically different diphenylmethyl-benzoyl triplet radical pair from 1a are substantially different from those observed with the diphenylmethyl-acyl radical pairs from adamantyl ketones 1b-d. While the solution and solid-state kinetics of triplet radical pairs from ketone 1a are very similar, with lifetimes that vary from 1.3 to 1.5  $\mu$ s, the corresponding values in the case of 1b-d change from 1.2  $\mu$ s in solution to short- and long-lived components of 2.3 and 53  $\mu$ s for 1b, 3.5 and 61  $\mu$ s for 1c, and 1.8 and 63  $\mu$ s for 1d, respectively.



**Figure 4.** Transient absorption spectra of 1-((1R,3R,5R,7R))-adamantan-2-yl)-2,2-diphenylethan-1-one (1c) in acetonitrile solution (top) and in aqueous nanocrystalline suspension (bottom). The fitted exponential decay curves in the insets were used to determine the lifetimes of the transient absorption signals.

We were able to confirm that the short-lived component observed with nanocrystalline suspensions does not originate from a small amount of the sample in solution. The observed transient and the decay kinetics were not affected by oxygen, which would have trapped free radicals in solution. Furthermore, a <sup>1</sup>H NMR analysis of recovered samples showed only the starting material. It is possible that the short-lived component may arise from molecules in less rigid sites either at the surface or at defect sites, but we cannot discount that different triplet radical pair sublevels formed by state-selective intersystem crossing in the starting ketone may have access to different intersystem crossing mechanisms.<sup>33–38</sup>

The first key observation from the data shown in Table 1 is the remarkable difference between the phenylacyl (benzoyl) radical pair in 1a and the alkyl-acyl radical pairs in 1b-d. The second most notable observation pertains to the unprecedented long lifetime for an acyl-containing radical pair state. We will center our attention on the long-lived ca. 50–60  $\mu$ s components for ketones 1b-d, which account for the majority of the transients formed, and compare them with solution and gas-phase decarbonylation lifetimes drawn from the literature for analogous acyl radicals<sup>26,27</sup> (Table 1). An important conclusion from ketone 1d is that the rate of decarbonylation in the solid state is much slower than that in solution. This can be shown by comparing the decarbonylation rate of 1.9  $\mu$ s in solution with a time constant for intersystem crossing of 63  $\mu$ s in the crystalline state. Given that no photoproducts are observed by <sup>1</sup>H NMR, we take an upper bound of 1% decarbonylation to estimate a lower bound for the time constant of this bond-cleavage reaction. This analysis assumes that each molecule in the sample accesses the <sup>3</sup>RP-1 state at least once, which we believe to be a conservative estimate on the basis of a comparison with an analogous sample of dicumyl

ketone (with a known solid-state quantum yield of  $\Phi = 0.2$ ), which is completely converted to the corresponding photoproduct under the same experimental conditions. If our assumption holds, the time constant for the decarbonylation reaction (step 4, Scheme 1) must be at least 2 orders of magnitude greater than that of the intersystem crossing step 5 in Scheme 1. Thus, a long-lived transient with a time constant of 63  $\mu$ s for the decay of the radical pair from 1d implies a decarbonylation time constant of at least 6.3 ms. This lowerbound value demonstrates that the crystalline solid state can drastically lengthen the decarbonylation lifetime by more than 3 orders of magnitude.

The lifetime enhancement observed in the solid state for the radical pairs featuring aliphatic acyl radicals (1b-d) is consistent with reports of restricted radical pairs and biradicals exhibiting longer lifetimes in the solid state than in solution.<sup>39-43</sup> The structural rigidity and least-motion character of reactions in solids suggested by the topochemical postulate<sup>44</sup> suggest that it is reasonable to analyze the lifetime enhancement in terms of structural parameters of the ketone molecular and crystal structure.<sup>45,46</sup> Thus, on the assumption that the acyl radical resides in an sp<sup>2</sup> orbital, the two singly occupied orbitals would remain in the original orientation of the  $\sigma$  bond after the  $\alpha$ -cleavage step, coaligned and close to the ketone  $\alpha$  bond length distance of 1.54 Å. As mentioned before and suggested in Figures 1 and 2, the proximity of the two radical centers is expected to result in large zero-field splitting and a large singlet-triplet energy gap. When we consider that energy must be conserved when there is a change in spin angular momentum, the large energy gap between singlet and triplet states poses a challenge for the intersystem crossing step. Furthermore, on consideration that the open-shell singlet should be ideally poised for bond formation, it is reasonable to expect that dephasing and equilibration between the  $T_0$  and S radical pair states, potentially facilitated by the relatively different g factors of the two radical centers, should be very unlikely. An alternative mechanism based on coupled electron-nuclear spin flips determined by hyperfine coupling (hfc) interactions are known to be effective when the S-T gap is relatively small, at relatively long inter-radical distances. Spin-flipping mechanisms caused by the dynamic modulation of magnetic fields through spin-lattice relaxation requires fast molecular dynamics, such as spin-rotation interactions and solvent motion,<sup>47,48</sup> which are ineffective under the rigidity of the crystal lattice. Finally, while it may be expected that the most efficient ISC mechanism for a triplet radical pair in a crystalline solid will be based on spin-orbit coupling (SOC), it is anticipated that the collinear arrangement of the two singly occupied orbitals will be unfavorable, as there is a limited change in angular momentum mediated by electron exchange and/or mixing of zwitterionic states.<sup>15–17</sup> While there is much work to be done to ascertain the initial polarization, spin sublevel equilibration, and relative contributions of the different ISC mechanisms, it is clear that the restrictions imposed by the crystal lattice are able to maintain these spin systems for much longer times in comparison to any other medium. To the best of our knowledge, the long-lived component of the <sup>3</sup>RP-1 state of ketones 1b-d (53-63  $\mu$ s) has the longest lifetimes for an acyl-alkyl triplet biradical or radical pair reported to date, with previous lifetimes reaching no more than ca. 5.5  $\mu$ s.<sup>29,49-54</sup> Further studies based on magnetic resonance methods such as CIDEP will yield

# CONCLUSION

Using four ketones with a diphenylmethyl group on one side and either phenyl or alkyl groups derived from adamantane on the other, the lifetimes of acyl-alkyl radical pairs in the crystalline solid state were measured for the first time. It was shown that the crystal lattice environment substantially enhances the lifetime of the triplet radical pairs, as they remain entangled by over 1 order of magnitude in comparison to analogous biradicals in solution. On the assumption that the formation of a  $\sigma$  bond occurs as soon as the singlet radical pairs are formed, the long triplet radical pair lifetimes highlight the importance of molecular and solvent dynamics on the rate and efficiency of ISC mechanisms. While these results are extremely interesting and promising within the context of quantum information systems, it will be essential to explore the complementary magnetic detection and analysis of the triplet radical pairs<sup>24</sup> to confirm the multiplicity of the optical signal carriers and their polarization and spin dynamics, including the unlikely possibility of reversible triplet-singlet dephasing mediated by the different g factors of the acyl and alkyl radical centers. These studies will take advantage of magnetic resonance methods, including chemically induced dynamic nuclear polarization (CIDEP).

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c03026.

General methods and synthesis procedures, spectroscopic <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR data for compounds 1a-d, UV-vis and transient absorption data for solutions and suspensions of 1a-d, characterization of suspensions by DLS and PXRD, <sup>1</sup>H NMR photoproduct analysis, and single-crystal X-ray thermal ellipsoid plots and crystallographic data for compound 1d (PDF)

## Accession Codes

CCDC 2071808 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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