

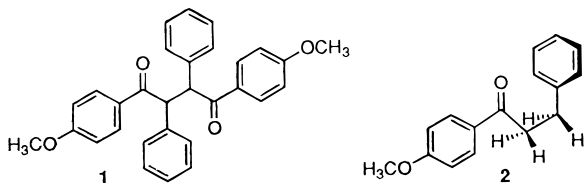
## Remarkable Discrimination in the Triplet Lifetimes of the Diastereomers of 1,4-Bis(*p*-methoxyphenyl)-2,3-diphenylbutan-1,4-dione

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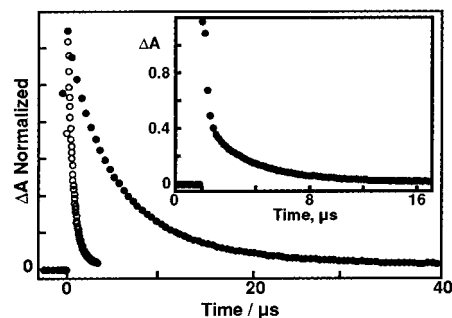
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Stereochemical control and chiral discrimination, in particular, are essential features in biological systems. One objective in supramolecular chemistry is to understand the functions of biological systems. In this context, photochemical probes are employed to characterize the properties of supramolecular structures and are used to study the dynamics of local mobility or complexation.<sup>1–3</sup> In order to study chirality in these structures, probes with a stereocenter that affects their photophysics are desirable. However, no photophysical probes with potential for enantio- or diastereomeric discrimination in solution have been reported. We describe herein a remarkable diastereomeric discrimination in the triplet lifetimes, *in solution*, of 1,4-bis(*p*-methoxyphenyl)-2,3-diphenylbutan-1,4-dione (**1**):



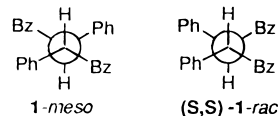
The role of charge transfer in ketone photoreductions by alkylbenzenes is well established.<sup>4,5</sup> Rapid intramolecular deactivation of  $n,\pi^*$  triplet states of ketones by the  $\beta$ -phenyl ring leads to very short lifetimes.<sup>6–13</sup> The introduction of a *p*-methoxy substituent can lead to state-switching, which causes the lowest triplet to have a  $\pi,\pi^*$  configuration with an upper  $n,\pi^*$  triplet close in energy.<sup>14,15</sup> In general, for ketones which undergo state-switching, the reactions typical of  $n,\pi^*$  triplets, e.g., Norrish type I and II, occur from the thermally populated triplet state.<sup>16,17</sup> This is true for **2**, for which the  $\beta$ -phenyl quenching of thermally populated  $n,\pi^*$  triplets increases the lifetime as compared to that for  $\beta$ -phenylpropiophenone.<sup>11</sup> In addition, studies with derivatives substituted on the  $\beta$ -phenyl ring have established the importance of charge transfer.<sup>13</sup> The



**Figure 1.** Triplet decay of **1-meso** (○) and **1-rac** (●) in methanol monitored at 400 nm. The inset shows the triplet decay for a solution containing **1-meso**:**1-rac** (4:1) in acetonitrile. The lifetimes for the fast and slow components were  $220 \pm 10$  ns and  $3.6 \pm 0.4$   $\mu$ s, respectively.

approach of the  $\beta$ -phenyl ring toward the carbonyl can be rate-limiting when the derivatives of **2** are incorporated in restricted environments; this property has been exploited to probe organized systems.<sup>18–25</sup> It is noteworthy that novel diastereomeric discrimination in the triplet lifetimes of *p*-methoxy- $\beta$ -phenylbutyrophenone has been observed in the solid state (racemic vs pure *R* or pure *S* crystals), while no discrimination was observed in solution.<sup>26</sup>

The diastereomers of **1** were synthesized following the procedure reported for analogous derivatives.<sup>27</sup> The stereochemical assignments were based on the comparison of the characteristic <sup>1</sup>H NMR resonances of the tertiary benzylic protons of **1-rac** ( $\delta$  5.32) and **1-meso** ( $\delta$  5.71) with those documented for 1,2,3,4-tetraphenylbutan-1,4-dione.<sup>28,29</sup>



The transient absorption spectra obtained by laser flash photolysis<sup>30,31</sup> were similar for both diastereomers and were assigned to the triplet state by comparison with spectra reported for  $\beta$ -phenyl ketones.<sup>10,11,32</sup> This assignment was further supported by the quenching of the transient of **1** by oxygen ( $k_q \approx 5 \times 10^9$   $M^{-1} s^{-1}$  in acetonitrile) and 1-methylnaphthalene ( $k_q \approx 8 \times 10^9$   $M^{-1} s^{-1}$ ).<sup>33</sup> The triplet decays were first-order (Figure 1), and the lifetimes for **1-meso** were shorter than those for **1-rac** (Table 1). Self-quenching was observed only for **1-rac** ( $4 \times 10^8$   $M^{-1} s^{-1}$  in acetonitrile). Furthermore, the triplet decay for samples containing different ratios of **1-rac** and **1-meso** were biphasic (Figure 1; inset), and the two lifetimes were close to

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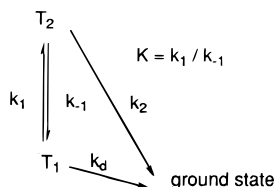
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**Table 1.** Triplet Lifetimes ( $\mu\text{s}$ ) of the  $\beta$ -Phenyl Ketones

ketone	carbon tetrachloride	methanol	acetonitrile
<b>1-rac</b> <sup>a</sup>	>1.0 <sup>c</sup>	>6.0 <sup>c</sup>	>5.0 <sup>c</sup>
<b>1-meso</b> <sup>a</sup>	0.10	0.60	0.20
<b>2</b> <sup>b</sup>		0.24	0.05

<sup>a</sup> Determined in deaerated samples ( $1-2 \times 10^{-4}$  M) at 400 nm; error  $\pm 10\%$ . <sup>b</sup> Reference 32; error  $\pm 5\%$ . <sup>c</sup> Corresponds to minimum values, since self-quenching occurs.

**Scheme 1**

those measured for the individual diastereomers.<sup>34</sup> This behavior shows that the difference in lifetimes is due to intrinsic properties of the diastereomers and not due to artifacts. If the difference in lifetimes was solely due to an impurity, one would observe for the mixture a single exponential decay with a lifetime longer than that observed for pure **1-meso**.<sup>35</sup>

In light of these considerations, the observed differences in the triplet lifetimes should be sought from the conformational preferences and the differences in the spatial orientation between the  $\beta$ -phenyl rings and the *p*-methoxybenzoyl moieties for the two diastereomers. From molecular mechanics calculations,<sup>36</sup> the lowest energy conformers for both diastereomers were found to be the ones with **h-anti** arrangement. The energy difference between the most stable **h-anti** conformations and the other staggered conformers are calculated to be  $2.8 \pm 0.1$  and  $1.9 \pm 0.06$  kcal/mol for **1-meso** and **1-rac**, respectively.<sup>37</sup> These differences are significant to ensure excitation of a predominant population of the molecules from the most stable **h-anti** conformations. We now employ the thermal equilibrium model<sup>11,16,17,38</sup> (Scheme 1) to understand the photophysics of **1**. Assuming that similar energy differences as those calculated for ground state ketones **1** apply in the triplet-excited states, the triplets will primarily exist in **h-anti** conformations in both  $T_1$  and  $T_2$  states. Moreover, for most of the triplet lifetime, the excited states will remain in the  $T_1$  state and undergo free bond rotations. However, the lifetime of the ketones in the  $T_2$  state will be limited by rapid deactivation ( $k_{-1} + k_2$ ) which competes with bond rotation. Thus, under the conditions of rapid equilibrium ( $k_1 \gg k_d$  and  $k_{-1} \gg k_2$ ) and the assumption that  $[T_2] \ll [T_1]$ , the triplet decay will follow first-order kinetics with a lifetime ( $\tau_{\text{obsd}}$ ) determined by the sum of the rates of deactivation from each state taking into account the fractional concentrations of  $T_1$  and  $T_2$  according to the equation  $1/\tau_{\text{obsd}} = Kk_2 + k_d$ .

The differences in the lifetimes of **1-rac** and **1-meso** can now be explained by considering the relative contributions of the deactivations from  $T_1$  and  $T_2$  for each diastereomer. For **1-meso**, the  $\beta$ -phenyl ring is *gauche* to the carbonyl moiety for most molecules that are thermally populated from  $T_1$  to the  $T_2$  state. Consequently,  $\beta$ -phenyl quenching can compete with deactivation back to  $T_1$  and the overall lifetime will be determined by the term  $Kk_2$ . On the other hand, the  $\beta$ -phenyl quenching is completely shut down for **1-rac** by virtue of the distal relation-

ship between the  $\beta$ -phenyl rings and the *p*-methoxybenzoyl moieties of the triplet-excited **h-anti** conformer. Indeed, a calculated torsional barrier of  $5.4 \pm 0.5$  kcal/mol must be overcome within the lifetime of  $T_2$  before the *gauche* relationship, a prerequisite for quenching, is established. Thus, the overall lifetime will be determined by the intrinsic decay  $k_d$ . This is supported by the fact that the lifetime for **1-rac** is comparable to that observed for *p*-methoxypropiofenone.<sup>10</sup>

One important aspect concerning the  $\beta$ -phenyl quenching is whether or not an eclipsed geometry between the carbonyl group and the phenyl ring is necessary or a mere “*gauche*” relationship would suffice. We have determined the experimental activation energies for the decay of **1-meso** in acetonitrile and methanol:  $6.6 \pm 0.2$  and  $6.3 \pm 0.2$  kcal/mol.<sup>39</sup> These values are higher than 4.3 kcal/mol determined for **2** in methanol<sup>11</sup> and account for longer lifetimes for **1**. Insofar as the energy spacing between  $T_1$  and  $T_2$  states of **1** is comparable to that in **2**, the reason for increase in the activation energy should be accounted for by the increase in barrier in moving away from the “*gauche*” conformation to the “quenching conformation”. The pre-exponential factors have to be taken into account to explain why the increase in lifetime is small based on the differences in activation energies. A larger pre-exponential factor is observed for **1-meso** ( $11.0 \pm 0.4$ ) when compared to that of **2** ( $9.8 \pm 0.3$ ),<sup>11</sup> suggesting that less reorganization is necessary to achieve the transition state for quenching in the former.

Rapid intramolecular energy transfer and self-quenching have been reported for analogous diketones.<sup>40</sup> For **1**, the energy transfer operates in both diastereomers such that each carbonyl group is excited for half of the time until deactivation occurs and, hence, cannot be responsible for the observed differences. That the self-quenching may influence the lifetimes to a minor extent, if any, comes from two considerations. First, whereas the self-quenching rate constant for the closely related 1,2-dibenzoylthane with lowest  $n,\pi^*$  triplet-excited state has been reported to be  $1.7 \times 10^7$  s<sup>-1</sup>,<sup>40</sup> the short triplet lifetime (<2 ns) for  $\beta$ -phenyl-propiofenone<sup>11</sup> leads to a rate constant larger than  $5 \times 10^8$  s<sup>-1</sup> for charge-transfer quenching. Thus, in a direct competition, the  $\beta$ -phenyl quenching must be favored over self-quenching. Second, if the deactivation occurs for both diastereomers from  $T_2$  states populated in the **h-anti** conformation, self-quenching would be more favored in **1-rac** because of the “*gauche*” relationship between the two ketone groups. Therefore, the lifetime for **1-rac** would be expected to be shorter than for **1-meso**, which is contrary to the observed lifetimes.

In summary, the diastereomeric discrimination observed in the lifetimes for **1-meso** and **1-rac** is a direct consequence of conformational control. This is akin to the stereochemical control in Norrish type II hydrogen abstractions<sup>41,42</sup> and solid-state photoreactions,<sup>43</sup> but has been observed for the first time in direct kinetic studies. The remarkable feature for **1** is that the discrimination is very efficient in solution, and this makes **1** potential probes to study the chirality of supramolecular structures.

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**Supporting Information Available:** Description of the MM2 calculations (3 pages). See any current masthead page for ordering and Internet access instructions.

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(34) Decays were recorded for 4 and 20  $\mu\text{s}$  to better define the fast and slow components and were fitted to the sum of two exponentials.

(35) The total concentrations of **1** for the mixtures and pure diastereomers were the same.

(36) MM2 calculations were performed on a CaChe work system. Details are given in the Supporting Information.

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