Intramolecular T_2-Energy Transfer from Anthryl Group Studied by Stepwise Two-Color Two-Photon Excitation: A Cis to Trans Isomerization and a Valence Isomerization

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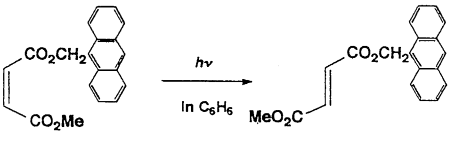
Intramolecular energy transfer from the second triplet of anthracene moiety is exemplified in the cis to trans isomerization of methyl maleate and the valence isomerization of norbornadiene to quadricyclane by stepwise two-color two-photon excitation method.

The second excited triplet (T_2) state of dibromoanthracene is known to have a triplet energy of about 72 kcal/mol[1] with short lifetime (about 0.25 ps[2a] - 200 ps[2b,c]). The T_2-states of other substituted anthracenes have roughly similar triplet energies and such short lifetimes and they can sensitize some reactions with poorer efficiencies.[1,2b] In addition to such short lifetime, anthracene and its mono substituted derivatives cannot be used as sensitizers because of their competing photodimerizations. If the intramolecular energy transfer is available, the efficiency of the T_2-sensitization may increase and the dimerization may be suppressed. We have recently shown an asymmetric synthesis (91% e.e.) of spirocyclopropane-1,9'-fluorene derivatives using anthryl group as an intramolecular sensitizer.[3a] The energy transfer from the T_2-state of the anthryl group is firmly shown by stepwise two-color two-photon excitation technique.[3b,c] Although the intramolecular energy transfer from T_2-state of anthryl group seems to be quite general and applicable to many photochemical reactions, such studies with clear-cut evidence in other systems have not been reported.[4]

We have previously reported a photochemical isomerization of (9-anthryl)methyl methyl maleate (**1**) to the corresponding fumarate (**2**).[5] The $S_1 \rightarrow S_1$ or $T_1 \rightarrow T_1$ energy transfer from the anthryl group to the maleate moiety is highly endothermic. Electron transfer process is also highly endothermic.[6] For this reason, Schenck type sensitization with the fast and reversible bond formation between the excited anthryl and the maleate moieties was proposed. The reactive state of anthryl group is assumed to be mainly the lowest triplet (T_1) state because the isomerization is considerably quenched by the dissolved oxygen (82% quenching at $[O_2] = 1.9 \times 10^{-3}$ M) under aerated conditions. However, if the T_1 state is a sole reactive state, the higher (> 99.9%) quenching should be observed, indicating the existence of additional channels leading to the same product via shorter lived excited states. In order to test the generality of the T_2-sensitization method, we report the examination of photoreaction of **1** and an additional application to the well-known isomerization of norbornadiene to quadricyclane using the stepwise two-color two-photon excitation method.

As previously reported, irradiation of a benzene solution of **1** under an inert atmosphere exclusively gave (9-anthrylmethyl)-fumarate (**2**) with quantum yield of 0.020 under deaerated conditions and 0.0035 under aerated conditions.[5] Irradiation of **2** does not afford **1** and the prolonged irradiation of **1** or **2** gives a Diels-Alder type cycloadduct with the poorer efficiency. (9-Anthryl)methyl norbornadiene-2-carboxylate (**3**) was synthesized in high yield by the condensation of the corresponding carboxylic acid and 9-anthrylmethanol in the presence of an equimolar amount of dicyclohexylcarbodiimide (DCC) in dichloromethane. The valence isomerization of norbornadiene to quadricyclane is well known to proceed by the direct or sensitized conditions.[7] The triplet energy of norbornadiene is estimated to be about 72[8] or 61[9] kcal/mol. The energy transfer from the T_1-state (42 kcal/mol) of the anthryl group is therefore highly endothermic. The energy transfer from the S_1-state is also highly endothermic since norbornadiene or its carboxylated derivative does not have strong absorptions at longer wavelength than 300 nm (ca. > 19 kcal/mol endothermic, anthryl S_1-state: 76 kcal/mol). The conceivable electron transfer process is also highly endothermic.[6] However, irradiation of a benzene solution of **3** with a 100-W Hg lamp for 1 h through a Pyrex filter under a nitrogen atmosphere produced (9-anthryl)methyl quadricyclane-2-carboxylate (**4**)[10] in 55% yield with the recovery of **3** in 32% yield. The conceivable anthracene dimer type compound(s) was not produced. The quantum yield of this isomerization is determined to be 0.029 under argon. The isomerization is hardly quenched by the dissolved oxygen under air (quantum yield = 0.022). This indicates the presence of a short lived reactive excited state. From the above mentioned reasons, these reactions may proceed via T_2-state of the anthryl group. The T_2-energy transfer processes are exothermic for both **1** and **3**.

In order to obtain evidence of the T_2-sensitization, flash photolysis experiments were carried out using stepwise two-color



1 **2**

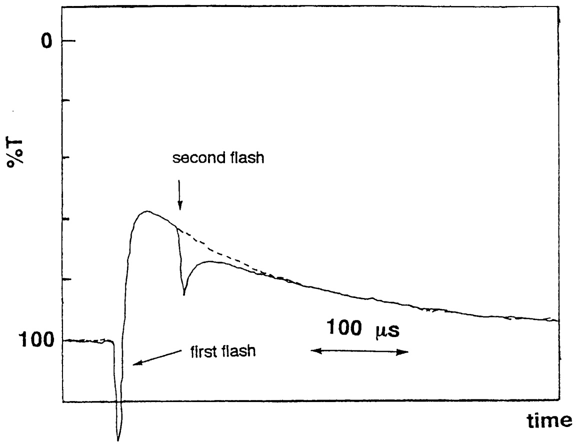
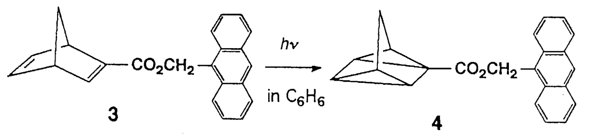


Figure 1. T_1-decay (transmittance scale) in stepwise two photon excitation of **1**. Dotted line shows the decay without second flash.



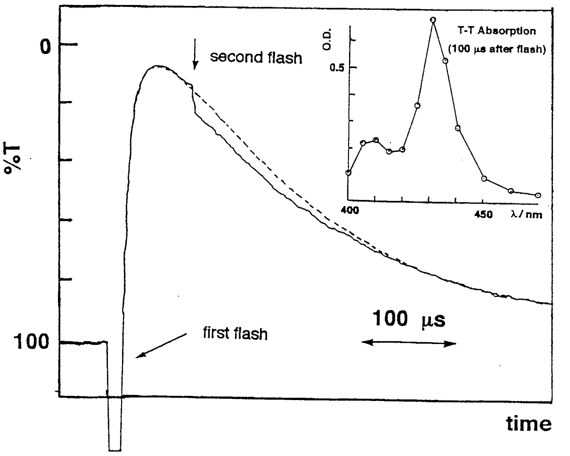


Figure 2. T_1-decay (transmittance scale) in stepwise two photon excitation of **3**. Dotted line shows the decay without second flash. T-T absorption of **3** is inserted.

two-photon excitation technique. The demonstration of the T_2-sensitization is based on the following photophysical processes and considerations: 1) direct irradiation (260 - 390 nm) of the substrate **1** or **3** by the first flash gives the long-lived T_1 state of the anthryl group after the intersystem crossing, 2) the second flash excitation (> 410 nm) of the long-lived T_1 state pumps up to the T_n state giving the short-lived T_2 state after the very fast $T_n \rightarrow T_2$ internal conversion,[2a] 3) if the sensitization or energy transfer does not occur from the T_2 state, all the T_1 state will be regenerated (T_1 population does not change)[11]; however, if the sensitization or energy transfer occurs from T_2 state, a part of T_1 state cannot be recovered and the T_1-population decreases. 4) As a result, T_2-sensitization or energy transfer can be evidenced by judging whether there is a leak in the T_1 regeneration or not.

Figure 1 shows such an experiment for the isomerization of **1** to **2**. The y axis of Figure 1 is expressed as transmittance of triplet absorption (%T) at 430 nm. %T increases as T_1-population decreases. From the figure, it is clear that the T_1-population suddenly drops after the second flash. Figure 2 shows a similar kinetic profile for the excitation of **3**. Again, a drop of the T_1-population after the second flash was observed. Theses experiments clearly show the existence of energy consuming path (energy transfer or sensitization) in the higher excited triplet state (T_2) of the anthryl group. Thus, the T_2-state is most reasonably assigned to the reactive state for the observed reaction.[12] The produced triplet maleate or norbornadiene undergoes the isomerization as previously established.[7,13]

The present study successfully showed two examples of the intramolecular anthryl (T_2)-sensitization using the stepwise two-color two-photon excitation technique. This technique is shown to be very useful in the complex reaction as in the case of **1** where the two mechanisms are competing. Since the selected systems are not particular ones, the intramolecular anthryl (T_2)-sensitization method should have wide applicability. An advantage of this sensitization method is worthy to comment: the T_2-energy of anthryl group can be transferred only to close chromophore(s) because of the very short lifetime. For this reason, this method may be used in selective sensitization in bi- or multi-chromophoric photochemical systems and such studies will be planned.

References and Notes

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6 Electron transfer process is unlikely since the S_1 state of anthracene can reduce compounds whose reduction potentials are higher than -1.20 V vs S.C.E. The other excited states (T_1 or T_2) can reduce compounds with much higher reduction potentials. The reduction potentials of dimethyl maleate and methyl norbornadiene-2-carboxylate are -1.98 V (peak potential) and -2.56 V (peak potential) vs S.C.E (in CH_3CN, electrolyte: tetrabutylammonium perchlorate).

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10 mp. 139°C, MS (EI) m/z 326 (M^+), ^1H-NMR (100 MHz in $CDCl_3$) δ = 1.45-1.67 (m, 2H), 1.90-2.00 (m, 1H), 2.00-2.11 (m, 2H), 2.19-2.28 (m, 1H), 2.33-2.43 (m, 1H), 6.12 (s, 2H), 7.38-7.66 (m, 4H), 7.95-8.06 (m, 2H), 8.13-8.47 (m, 3H).

11 The efficiency of conceivable T_2-S_1 inverse intersystem crossing may be negligibly small in this case according to our previous study[2a] showing that the inverse intersystem crossing for anthracene or 9-methylanthracene occurs with very low efficiency ($1/10^4$, far smaller than the observed drop in T_1-population), however the process occurs with comparable efficiency (1/10) for 9,10-dibromoanthracene by heavy atom effect.

12 Although direct proof of the hypothesis that the drop in T_1-population is due to the observed reaction is not presented in this paper, the extent of the drop of T_1-population after the second flash (21% for **1**, 26% for **3**) is reasonable for the observed quantum yields (10^{-2} order), since we have observed a similar extent of drop (10-30%) under the similar conditions in the isomerization of spirocyclopropanefluorene derivative (quantum yield 0.073) where the hypothesis that the T_1-population drop is due to the isomerization was more firmly proved by the eosin sensitized stepwise two photon excitation and the detailed kinetic treatment.[3b] The above consideration is compatible with the fact that the eosin sensitized irradiation [with stationary irradiation (>500 nm) using a mixed solvent: ethanol-benzene (1:1)] of **3** never produce **4** even after 5 h irradiation].

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