November, 1992] © 1992 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 65, 3177—3179 (1992) 3177

Triplet Sensitized Quadricyclane-Norbornadiene Valence Isomerization of Methyl 5-(4-Biphenylyl)tetracyclo-[3.2.0.^{2,7}0.^{4,6}] heptane-1-carboxylate

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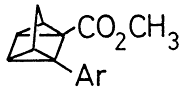
(Received April 27, 1992)

Synopsis. The mechanism of valence isomerization between methyl 5-(4-biphenylyl) tetracyclo [3.2.0.^{2,7}0.^{4,6}] heptane-1-carboxylate (**1**) and methyl 3-(4-biphenylyl)bicyclo [2.2.1]hepta-2,5-diene-2-carboxylate (**2**) under the triplet sensitization in benzene was studied by γ-radiolysis and pulse radiolysis. As an intermediate for the isomerization, an equilibrium state between a 1,3-biradical intermediate and a triplet state with the structure of norbornadiene has been estimated. The triplet energy levels of **1** and **2** were determined to be 59 and 57 kcal mol^{-1}, respectively. The energy difference between the ground states of **1** and **2** was determined to be 18 kcal mol^{-1}.

A valence isomerization between quadricyclane (Q) and norbornadiene (N) has received considerable attention as a solar energy storage process.[1] A variety of valence isomerizations, including direct photolysis, triplet sensitization, photosensitization with a metal complex, and donor–acceptor interaction, have been studied. We have elucidated that the phenyl, 2-naphthyl and 1-naphthyl derivatives of Q undergo isomerization into the corresponding N via the triplet state by using γ-radiolysis and pulse radiolysis techniques.[2] It has already been found that the most stable structure of the key intermediate for the valence isomerization of Q and N derivatives via triplet state changes from a 1,3-biradical intermediate for the phenyl derivatives to a triplet with an N structure (1,2-biradical intermediate) for 1-naphthyl derivatives. In order to elucidate the relationship between aryl substituents on Q and the intermediate, we herein studied the triplet sensitized Q–N isomerization of biphenylyl derivatives of Q, methyl 5-(4-biphenylyl)tetracyclo[3.2.0.^{2,7}0.^{4,6}]heptane-1-carboxylate (**1**), in benzene in the presence of benzophenone (BP). As the model compound of olefinic part of N, we used methyl 3-biphenylyl-*trans*-propenoate (**3**). The norbornene derivative, methyl 3-(4-biphenylyl)bicyclo [2.2.1]hepta-2-ene-2-carboxylate (**4**), which is a cisoid planar compound, was used as a criterion for the assignment of the other transient species.



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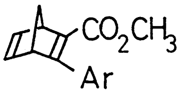

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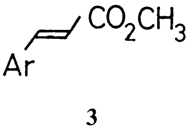

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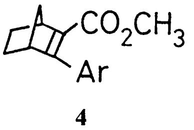

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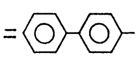


Results and Discussion

Triplet sensitization of **1** and methyl 3-(4-biphenylyl) tetracyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**2**) can be achieved by the γ-radiolysis or pulse radiolysis of benzene solutions in the presence of BP (the triplet energy, E_T=69 kcal mol^{-1}),[3] since the E_T values of **1** and **2** were determined by the phosphorescence spectra at 77 K to be 59 and 57 kcal mol^{-1}, respectively. The γ-radiolysis of **1** in benzene in the presence of BP readily gave **2**.[4] The ratio of **1** and **2** at the stationary state was found to be 19 : 81 in the presence of BP (Fig. 1). By the addition of azulene (Az), the ratio of **1** and **2** at the stationary state was changed to 4 : 96, which suggests the presence of a triplet intermediate quenchable by Az to **2**. The participation of the ionic species from **1** can be ruled out by the fact that the formation of **2** was not affected by the addition of an ion scavenger, such as butyl chloride.

It is well known that the pulse radiolysis of a benzene solution is an excellent method to give the triplet state of the solute.[5] Triplet sensitization of **1**—**4** has been carried out by nanosecond pulse radiolysis of the

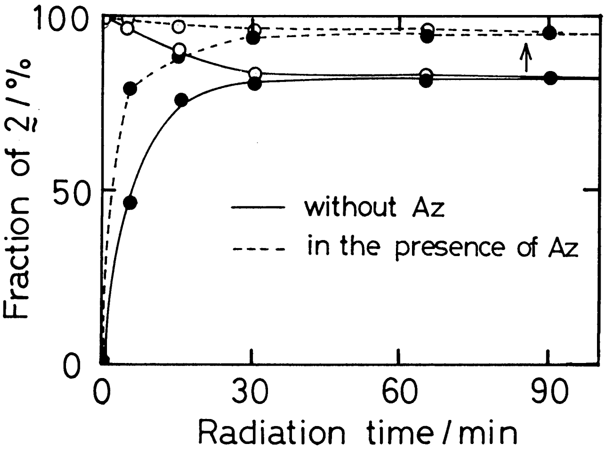


Fig. 1. Time conversion curves of **1** and **2** in deaerated benzene solutions in the presence of BP (solid line) and in the presence of both BP and Az (pointed line) after γ-radiolysis; [**1**], [**2**]=5 mmol dm^{-3}, [BP]=100 mmol dm^{-3}, [Az]=20 mmol dm^{-3}.

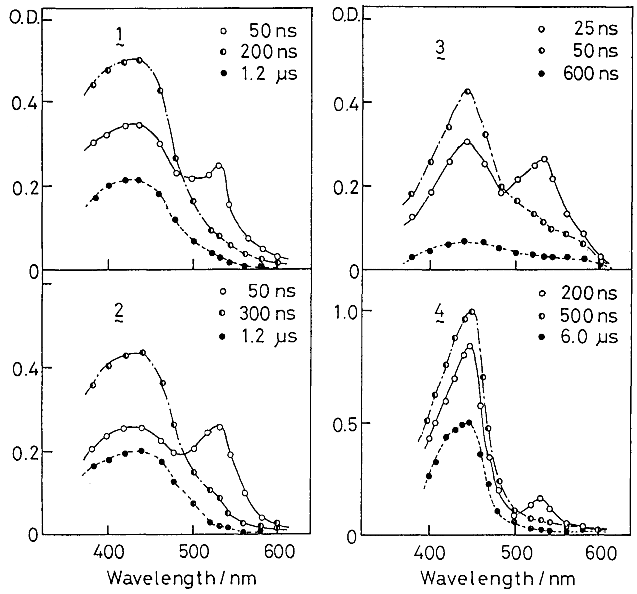


Fig. 2. Transient absorption spectra obtained at various times after an 8-ns pulse irradiation of benzene solutions of BP (20 mmol dm^{-3}) and **1**—**4** (2 mmol dm^{-3}) at room temperature.

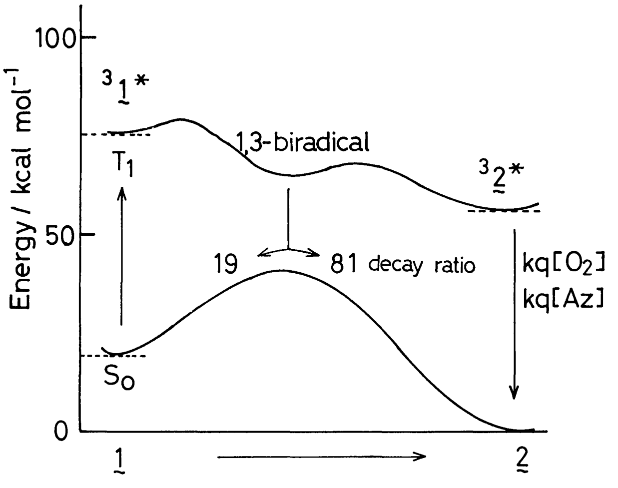


Fig. 3. Schematic potential energy surface for valence isomerization of **1** to **2** via the triplet state.

degassed benzene solutions in the presence of BP. The transient absorption spectra were recorded at various times after an 8-ns electron pulse. The results for **1**—**4** are shown in Fig. 2.

In the cases of **1** and **2**, quite similar results were observed. A transient absorption band at 530 nm due to the excited triplet state of BP was observed after an electron pulse irradiation and decreased with an increase in a broad peak at 440 nm. In the cases of **3** and **4**, rather sharp new absorption bands were observed at 440 and 445 nm, respectively. The ε_{max} value of the triplet state of **4** was estimated to be 3.5×10^5dm^2 mol^{-1} by means of the ε_{max} value of triplet BP.[6]

In the cases of **1** and **2**, the transient band at 440 nm (τ=1.3 μs) can be assigned to the excited triplet state of **2** (or 1,2-biradical intermediate of **2**) from the following observations: (i) The band is very close to that of the cisoid planar model (**4**; λ_{max} 445 nm, τ=12.8 μs). (ii) Since the band is quite different from that of a biphenylylmethyl radical (λ_{max}=326 nm),[7] the band at 440 nm is not due to the 1,3-biradical of **1**. If the common intermediate is a "tight 1,2-biradical", the absorption band should be shifted to a longer wavelength than that of **4**. (iii) Moreover, the band at 440 nm was quenched by oxygen (E_T=23kcal mol^{-1}; kq=4.1×10^9 dm^3 mol^{-1} s^{-1} for **1** and 4.0×10^9 dm^3 mol^{-1} s^{-1} for **2**) and azulene (E_T=39.8kcal mol^{-1};[8] kq=2.3×10^9 dm^3 mol^{-1} s^{-1} for **1** and 2.1×10^9 dm^3 mol^{-1} s^{-1} for **2**). If the band at 440 nm is due to a 1,3-biradical intermediate, such an efficient quenching by azulene could not occur. This is because the T_1-S_0 energy gap of the 1,3-biradical is nomally less than that of azulene.[9] Since the band at 440 nm appeared as a broad band compared with a 445 nm band of **4**, the conformational relaxation of a tight 1,2-biradical intermediate was presumed. Inefficient isomerization from **2** to **1** and the effects of added Az on the stationary ratio **2**/**1** indicates the presence of a 1,3-biradical intermediate which could not be detected, probably due to the short lifetime. The decay ratio of the 1,3-biradical into **1** and **2** might be 19 : 81. Therefore, the equilibrium between 1,2-biradical intermediate and 1, 3-biradical intermediate is concluded to exist on the triplet energy surface of **1** and **2**. The energy gap between the excited triplet states of **1** and **2** was calculated to be ca. 20 kcal mol^{-1} using the E_T values and strain energy difference (18 kcal mol^{-1}) obtained from a DSC measurement. On the basis of these results, the following schematic potential energy surface can be depicted (Fig. 3).

In the transient absorption spectra of **3**, the absorption band with a λ_{max} at 440 nm is associated with the planar triplet by a comparison with that of **4**. The short lifetime (τ=80 ns) indicates the presence of a rapid decay process via a twisted form.

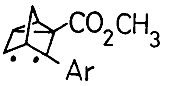
In order to clarify the factors which control the potential energy surface for the valence isomerization, the triplet sensitized *cis*–*trans* isomerization of **3** was investigated by γ-radiolysis in the presence of BP. The products were determined by HPLC. The *cis*–*trans* ratio of **3** at the stationary state was determined to be *cis*/*trans*=45/55. The addition of azulene (20 mmol dm^{-3}) enhanced the formation of the *trans* isomer (*cis*/*trans*=6/94), which supports the presence of *trans*-planar form as an equilibrium state.[9] From stationary experiments it is clear that an equilibrium state between a twisted form and a planar form in the stable intermediate of **3** existed, in agreement with the transient experiments.

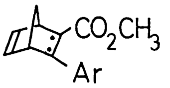
The valence isomerization between **1** and **2** via the triplet state was found to be correlated with the conformation of the corresponding olefinic analogue (**3**). The contribution of both a 1,3-biradical intermediate and a triplet state of N was estimated. Such a reactivity–conformation relationship is summarized in Table 1 along with previous results.[2b] The magnitude of the triplet energy of the aromatic substituent (Ar) seems to be one of the important factors which controls the

Table 1. Classification of Stable Intermediate between **1** and **2** and the Correlation with the Olefinic Moiety (**3**) via Triplet State

Substrate	Stable intermediate between **1** and **2**	Stable intermediate between *cis*-**3** and *trans*-**3**
Ar = Phenyl	1,3-BR[a]	Twist
Ar = Biphenylyl	1,3-BR $\rightleftharpoons$ 1,2-BR	Twist $\rightleftharpoons$ Planar
Ar = 2-Naphthyl	1,3-BR $\rightleftharpoons$ 1,2-BR	Twist $\rightleftharpoons$ Planar
Ar = 1-Naphthyl	1,2-BR[b]	Planar

a) 1,3-BR=1,3-biradical intermediate. b) 1,2-BR=1,2-biradical intermediate.





isomerization mechanism.

Experimental

Apparatus. The transient absorption spectra were measured using the L-band linear accelerator at Osaka University as the source of electron pulses. The energy was 28 MeV and the pulse width was selected to be 8 ns. The dose was 0.74 kGy per pulse and the beam diameter was ca. 4 mm. A 450 W xenon pulse lamp (OPG-450, Osram), a monochrometer (Nikon G-250), a photomultiplier tube (R-928), and a programmable digitizer (Tektronix 7912AD) were used. The system was controlled by computer. γ-Radiolysis in benzene was carried out in pyrex cells using a ^{60}Co source up to a dose of 0.49 kGy at room temperature. The phosphorescence spectra were recorded for an ether–isopentane–ethanol (5:5:2) solution at 77 K on a Shimadzu RF-501 spectrophotometer equipped with phosphorescence accessories. The energy difference between the ground states of **1** and **2** was measured using a Seiko Electric DSC-200/SSC5000 at different rising rates of temperature (2—5 °C min^{-1}).

Materials. The syntheses of **1**—**4** were performed according to the reported methods.[2b)] The structures of these compounds were satisfactorily confirmed by the spectral data. Benzophenone and azulene were purified by recrystallization from ethanol and sublimation, respectively. A spectral grade of benzene was used as a solvent. Solutions were freshly prepared before irradiation and were degassed under high vacuum.

We thank Dr. Sanyo Hamai of Miyazaki Medical College for his help in measuring the phosphorescence. We also thank Dr. Takahiro Seki, Research Institute for Polymers and Textiles, for his help and discussion concerning the DSC experiment. Finally, the authors wish to express their thanks to members of the Radiation Laboratory of ISIR for their running the linear accelerater.

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