

Intramolecular Long-Distance Electron Transfer and Triplet Energy Transfer. Photophysical and Photochemical Studies on a Norbornadiene–Steroid–Benzidine System

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Abstract: A bichromophoric compound 3 β -((2-(methoxycarbonyl)bicyclo-[2.2.1]hepta-2,5-diene-3-yl)carboxy)androst-5-en-17 β -yl-2,2',6,6',N,N,N',N' heptamethylbenzidine (N–S–B) was synthesized, and its photochemistry was examined by using both steady-state and time-resolved techniques. Intramolecular electron transfer from the singlet excited state of benzidine to the norbornadiene chromophore in N–S–B occurs with efficiency (Φ_{ET}) of ca. 12% and rate constant (k_{SET}) of ca. 1.1×10^7 s⁻¹, resulting in the singlet radical ion pair ¹(N^{•-}–S–B^{•+}) followed by intersystem crossing to the triplet state ³(N^{•-}–S–B^{•+}). Recombination of ³(N^{•-}–S–B^{•+}) yields triplet norbornadiene group. The efficiency ($\phi_{RIPISC} \cdot \phi_{RIPRC}$) of the formation of the triplet norbornadiene from the radical ion pair is ca. 17%. The singlet excited state of benzidine group in N–S–B undergoes intersystem crossing to its triplet state with efficiency (Φ_{ISC}) of ca. 56%. Intramolecular triplet energy transfer leading to the formation of the triplet norbornadiene chromophore is efficient ($\phi_{TT} =$ ca. 65%, $k_{TT} =$ ca. 5.2×10^5 s⁻¹). Selective excitation of the benzidine chromophore results in isomerization of the norbornadiene group to quadricyclane. This isomerization proceeds either via intramolecular triplet sensitization or radical-ion pair recombination mechanism. The long-distance intramolecular triplet energy transfer and singlet electron transfer are proposed to proceed via a through-bond mechanism.

Introduction

Photoinduced electron transfer and energy transfer play an important role in chemical and biochemical processes.¹ Electron transfer in general requires a proximity of the electron donor and acceptor comparable to their van der Waals radii. Similarly, triplet–triplet energy transfer proceeds via Dexter electron exchange interaction² and may be visualized in terms of two electron transfer processes or one electron transfer and one hole transfer processes.^{3,4} The rate constants both for electron transfer and Dexter energy transfer decrease exponentially with increasing the donor–acceptor distance. Thus, one might expect that the rate constants for electron transfer or triplet energy

transfer will become negligibly small as the donor–acceptor distance increases beyond the sum of their van der Waals radii. However, the evidences for long-distance electron transfer^{3–12} and triplet energy transfer^{13–17} with great efficiency in bichromophoric molecules in which the donor and acceptor are held

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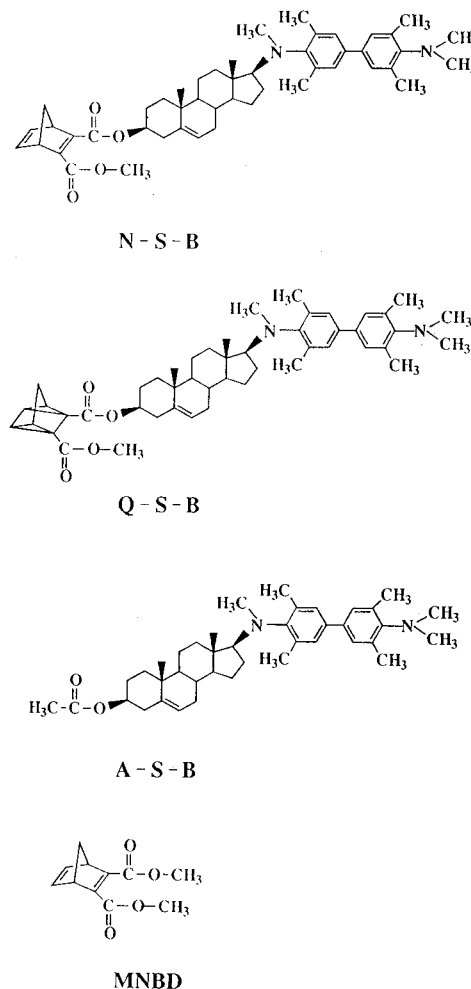
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at a effectively fixed separation by rigid molecular bridging frameworks have been accumulated. Closs and his co-workers³ studied the electron transfer in anions of bifunctional steroids A–S–B[−], where B is 4-biphenyl, S is a rigid saturated hydrocarbon spacer, and A is one of a series of different molecular groups. While in all cases the distance between A and B[−] is in excess of 10 Å, the maximum rate constants for intramolecular electron transfer reach 10⁹ s^{−1}. They also employed different rigid saturated spacer groups to separate electron donors and acceptors and to probe the effect of thermodynamic driving force, distance, solvent, and temperature on rate constants for electron transfer. Their work confirmed the existence of the Marcus inverted region and provided a theoretical foundation to guide experimentation. For molecules with dimethoxynaphthalene as the donor, 1,1-dicyanoethylene as the acceptor, and the rigid polycyclic norbornane structures as the spacers, Verhoeven, Paddon-Row, and their co-workers⁴ demonstrated the occurrence of very fast photoinduced electron transfer. They investigated the effects of the bridge configuration on the rate constant of intramolecular electron transfer and found that substitution of gauche for trans links in the spacer significantly decreased the electron transfer rate constants. Zimmt and Zeng⁵ employed similar molecule systems to demonstrate that electronic symmetry can modulate intramolecular electron transfer rate constants by at least 2 orders of magnitude. Gust, Moore, and their co-workers⁶ designed a series of multicomponent compounds after the model of the bacterial reaction center and studied their intramolecular electron transfer reaction. They revealed that molecules of this type can use the excitation energy effectively to produce intramolecular ion pairs with long lifetimes. Recently, Schuster and Zhu⁷ examined the photochemical reactions of an aryl azide group in an aryl amine-steroid-azide system in which the two chromophores are separated by 17.8 Å and found that the azide group is effectively activated by the remote amine group via long-distance electron transfer mechanism. More recently, Burrow, Jordan, and their co-workers⁸ studied the dissociation of Cl[−] from a molecule with ethylenic and C–Cl groups separated by a rigid nonconjugated bridge for 5.8 Å. Under low-energy electron impact the electron is initially captured into a π^* orbital localized on the ethylenic group, followed by efficient electron transfer to the σ^* orbital localized on the C–Cl group and subsequent dissociation. Similarly, long-distance intramolecular triplet energy transfer has also been examined.^{13–17} For the molecule 1-benzoyl-4-(2-naphthyl)bicyclo[2.2.2]octane in which the benzoyl (energy donor) and naphthyl (acceptor) spacing is fixed at ca. 7 Å, Zimmerman and Mcklevery¹³ found that the triplet energy transfer occurred with 100% efficiency. Using a rigid steroid spacer, which places the benzophenone (donor) and naphthalene (acceptor) chromophores at a distance of ca. 14 Å, Keller and Dolby¹⁴ found that triplet energy transfer efficiency is about 35%. For the molecule spiro[9,10-dihydro-9-oxoanthracene-10,2'-5',6'-benzindan] in which the anthrone (donor) and naphthalene (acceptor) moieties are rigidly linked and separated by ca. 5.1 Å, Weers, Rentzepis, and their co-workers¹⁵ determined the rate constant for triplet energy transfer to be about 3 × 10¹⁰ s^{−1}. More recently, Morrison and Wu¹⁶ studied the photochemistry of 3 α -(dimethylphenylsiloxy)-5 α -androstane-11,17-dione and 3 α -(dimethylphenylsiloxy)-5 α -androstane-17-one in which the dimethylphenylsiloxy (donor) and 17-keto (acceptor) groups are separated by 11.6 Å, and estimated the efficiency of the intramolecular triplet energy transfer having a minimum value of ca. 30%. In a preceding report we revealed that for a benzophenone–steroid–norbornadiene system where the benzophenone group (donor) and the

Chart 1



norbornadiene group (acceptor) are separated by ca. 10.8 Å, the efficiency and rate constant for the long-distance intramolecular triplet energy transfer were determined to be 22% and 1.5 × 10⁵ s^{−1} respectively.¹⁷ The high efficiency of the long-distance intramolecular electron transfer and triplet energy transfer that occurred in rigid bichromophoric molecules was rationalized by through-bond interactions of the donor and acceptor orbitals with those of the connecting σ bond relays. It has been revealed that the rate constants for electron transfer and energy transfer via through-bond mechanisms decreases exponentially with increasing the number of the bridging C–C σ bonds.³

Up to now, the majority of the studies for long-distance intramolecular electron transfer and triplet energy transfer have mainly concerned photophysical processes. There are only a few examples of application of through-bond electron transfer and triplet energy transfer to activation of remote acceptor groups for chemical reactions.^{7,8,16,17b} In the present work we study the photochemistry of the bichromophoric compound N–S–B shown in Chart 1. It has been established that norbornadiene and its derivatives can be photochemically converted into their valence isomers, quadricyclane, via triplet states.¹⁸ This reaction can be photoinitiated by a triplet sensitizer.¹⁹ Since the bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate group is a good electron acceptor, one can also use an electron donor to photosensitize its isomerization.²⁰ In this case the rearrangement mechanism of the norbornadiene involves

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electron transfer from the sensitizer to the norbornadiene, intersystem crossing of resultant radical-ion pairs and recombination of the radical-ion pairs to give norbornadiene triplets followed by rearrangement to the valence isomer. For N-S-B molecule, we could selectively excite the benzidine group. Long-distance triplet energy transfer activates the norbornadiene group and initiates its isomerization to quadricyclane. We also revealed the existence of long-distance electron transfer from the singlet excited state of benzidine to the norbornadiene, and this process initiates the later group isomerization via radical-ion pair recombination mechanism. The efficiencies and rate constants of the long-distance triplet energy transfer and electron transfer were examined by steady-state photolysis and time-resolved spectroscopy. These findings provide a new example of using an antenna chromophore to activate a remote functional group for chemical reaction via long-distance electron transfer and triplet energy transfer.

Results and Discussion

Synthesis of Norbornadiene-Steroid-Benzidine (N-S-B). The synthesis of N-S-B involved two steps. Reductive amination of 3 β -hydroxy-androst-5-en-17-one with 2,2',6,6',*N,N,N'*-heptamethylbenzidine yields a mixture^{7a,21} of the diastereomers 3 β -hydroxyandrost-5-en-17 β -yl-2,2',6,6',*N,N,N'*-heptamethylbenzidine (HO-S-17 β -B) and 3 β -hydroxyandrost-5-en-17 α -yl-2,2',6,6',*N,N,N'*-heptamethylbenzidine (HO-S-17 α -B) with a ratio close to 1:1. Assignments of HO-S-17 β -B as the 17-C- β amine and HO-S-17 α -B as the 17-C- α amine were supported by ¹H NMR resonance at 3.40 and 3.10 characteristic of 17-C- α H and 17-C- β H, respectively. The isomeric amines could be separated by chromatography. In the present work we only used HO-S-17 β -B as the starting material to prepare N-S-B by its esterification with 2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-carboxyl chloride.

Intramolecular Electron Transfer from the Singlet Excited State of the Benzidine to the Norbornadiene Chromophores in N-S-B. To search for evidence of ground state interactions between the donor benzidine and the acceptor norbornadiene groups in N-S-B, the absorption spectra of this compound and the models for the donor, 3 β -acetoxyandrost-5-en-17 β -benzidine (A-S-B, Chart 1), and for the acceptor, dimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-carboxylate (MNBD) in cyclohexane were examined. Table 1 gives the parameters of the absorption spectra together with those of the emission spectra and cyclic voltammetry for N-S-B, A-S-B, and MNBD. The absorption spectrum of N-S-B is essentially identical with the sum of the spectra of A-S-B and MNBD, suggesting the absence of measurable interaction between the benzidine and norbornadiene chromophores of N-S-B in ground state. Significantly, the absorption of A-S-B extends to longer wavelength than does that of MNBD. The energy of the singlet excited state of the benzidine chromophore (ca. 86 kcal/mol) is lower than that of MNBD (>95 kcal/mol), as estimated from the absorption spectra. Thus, singlet-singlet energy transfer

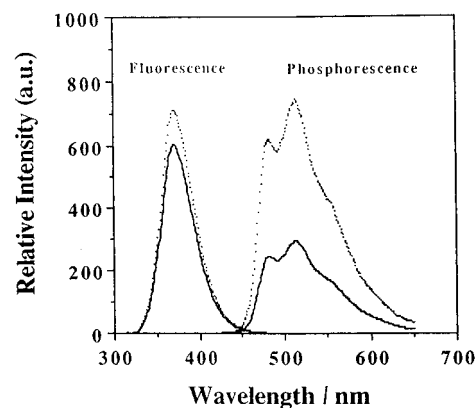


Figure 1. Emission spectra of N-S-B (—) and A-S-B (---). The fluorescence and phosphorescence spectra were obtained in cyclohexane at room temperature and in 2-methylhydrofuran at 77 K, respectively. $\lambda_{\text{ex}} = 300$ nm, [N-S-B] = [A-S-B] = 2×10^{-5} M.

from the excited benzidine chromophore to norbornadiene chromophore is impossible. Furthermore, this factor permits the selective excitation of the benzidine moiety in the bichromophoric compound N-S-B.

The fluorescence spectra of N-S-B and A-S-B in cyclohexane were studied and are given in Figure 1. Both compounds exhibit strong fluorescence. The parameters of the fluorescence spectra are given in Table 1. The general feature of these two spectra are essentially identical. However, the fluorescence efficiency of the benzidine chromophore in N-S-B is ca. 15% less than that in the model compound A-S-B. This observation indicates that quenching of the benzidine fluorescence by the norbornadiene group in N-S-B operates. Measurements at different concentrations reveal that the quenching is intramolecular. The fluorescence lifetimes for N-S-B and A-S-B were determined to be 10.8 and 12.2 ns, respectively (Table 1). These data allow the calculation of the quenching constant (k_{SET}) and the quantum yield (Φ_{SET}) of the quenching, which were obtained to be 1.1×10^7 s⁻¹ and 0.12, respectively. The value of the quenching efficiency thus obtained is comparable with that from the fluorescence efficiency measurements.

Since the possibility of singlet-singlet energy transfer responsible for the long-distance intramolecular quenching of the benzidine fluorescence by the norbornadiene group in N-S-B is excluded on thermodynamic grounds as mentioned above, we examined the reality of electron transfer between the two chromophores as the cause of the fluorescence quenching. The effects of solvent and distance on the thermodynamics of long-distance electron transfer have been analyzed by Weller²² and by Verhoeven, Paddon-Row, and their co-workers^{4a} as well as by Schuster.^{7a} The free energy change (ΔG) involved in an photostimulated electron transfer process can be estimated by eq 1

$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - \Delta E_{00} - e^2/\epsilon R_{\text{cc}} - e^2/2(1/r_+ + 1/r_-)(1/37 - 1/\epsilon) \quad (1)$$

where ΔE_{00} is the excited state energy, and in this case represents the singlet excited energy of the benzidine group (86 kcal/mol). $E_{\text{ox}}(\text{D})$ and $E_{\text{red}}(\text{A})$ are the redox potentials of the donor and acceptor, respectively, determined in acetonitrile solution. $e^2/\epsilon R_{\text{cc}}$ is the Coulombic interaction in the ion pair state whose magnitude depends on the distance between the donor and acceptor (R_{cc}) and on the dielectric constant (ϵ) of

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Table 1. Spectroscopic and Electrochemical Properties of Compounds

compd	absorption ^a		fluorescence ^a				phosphorescence ^c		E_{00} (kcal/mol)		redox potential ^e (V vs SCE)
	λ_{\max}	$\log \epsilon$	λ_{\max} (nm)	Φ_f^b	Φ_{ISC}^b	τ (ns)	λ_{\max} (nm)	τ^d (ns)	E_{00}^S	E_{00}^T	
N–S–B	290	3.55	370	0.11	0.56	10.8	485 514 556	1.25			
A–S–B	290	3.50	370	0.13	0.64	12.2	485 514 556	3.60	86	63	0.65 ± 0.03 (15.0 ± 0.7 kcal)
MNBD	250	3.96							>95	53	–1.67 to –1.77 (–38.5 to –40.8 kcal)

^a In cyclohexane. ^b Φ_f , Φ_{ISC} : Fluorescence and intersystem crossing quantum yields respectively. The value of Φ_{ISC} for N–S–B was obtained by $\Phi_{ISC}(N-S-B) = \Phi_{ISC}(A-S-B) \cdot \tau(N-S-B) / \tau(A-S-B)$, where $\tau(N-S-B)$ and $\tau(A-S-B)$ are the fluorescence lifetimes for N–S–B and A–S–B, respectively. ^c In glassy MTHF at 77 K. ^d Determined by T–T transient absorption. ^e In acetonitrile.

the medium separating the charges. The last term in eq 1 is the Born correction to the solvation energy which depends on the radius of the donor cation (r_+) and the acceptor anion (r_-). We used Alchemy II program to calculate the energies of the two general conformations, extended and bent, of N–S–B and found that the extended conformation has the lowest energy. In this conformation the center-to-center distance between the norbornadiene and benzidine groups, defined as the distance between the C-2 in norbornadiene and the center of the *Ph*–*Ph* bond in benzidine, is 17.0 Å. Thus, we set R_{cc} to equal to 17.0 Å for N–S–B. It is likely that other conformations of this molecule will be populated within the lifetime of the excited state of the benzidine group. However, analysis of eq 1 shows that at this distance small change in R_{cc} will result in only a minor impact on ΔG . To estimate the Born correction to the solvation energy we set r_+ and r_- equal to 6.7 and 3.6 Å, respectively, by assuming that both donor and acceptor are spherical. Cyclic voltammetric measurement of the model compound A–S–B in acetonitrile shows reversible oxidation waves with the oxidation potential ($E_{ox}(D)$) of 0.65 ± 0.03 V vs SCE. However, the electrochemical formation of the radical anion from MNBD is found to be irreversible in acetonitrile, indicating that secondary reactions are significant on the time scale of the electrochemical experiments. Thus, the value of its reduction potential ($E_{red}(A)$) is more approximate and was estimated from the cathodic peak potential to be –1.67 to –1.77 V vs SCE.^{4a} Calculation according to eq 1 reveals that electron transfer from the singlet excited benzidine portion of N–S–B to the norbornadiene group in cyclohexane ($\epsilon = 2.015$ D) is exothermic by 7–9 kcal/mol. Thus, we attributed the fluorescence quenching of the benzidine chromophore in N–S–B to the long-distance intramolecular electron transfer from the singlet excited benzidine to the norbornadiene group as shown in Scheme 1. This conclusion is supported by the results of flash photolysis measurements, as reported later.

Intramolecular Energy Transfer from the Triplet State of the Benzidine Chromophore to the Norbornadiene Group in N–S–B. Since N–S–B and A–S–B are very insoluble in nonpolar solvents such as isopentane at low temperature, we used 2-methyltetrahydrofuran (MTHF) as the solvent to study the phosphorescence emission of these compounds. Figure 1 gives the phosphorescence spectra of N–S–B and A–S–B in glassy MTHF at 77 K. Both spectra show distinct vibronic transitions. The phosphorescence efficiency of the benzidine group in N–S–B is ca. 60% less than that in A–S–B, suggesting that the triplet state of the benzidine chromophore in N–S–B is quenched by the norbornadiene group. We estimated the triplet energy of benzidine chromophore from the phosphorescence spectrum to be ca. 63 kcal/mol. The triplet energy of the norbornadiene group was reported to be 53 kcal/mol,^{20a} which is much lower than that of the benzidine group.

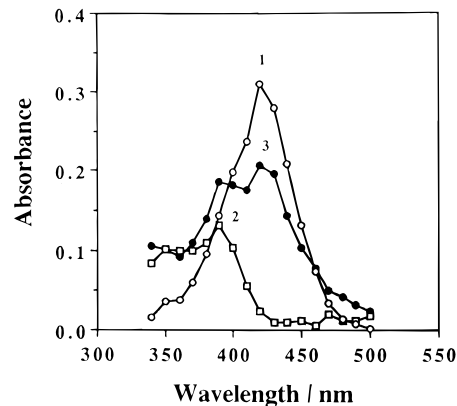


Figure 2. Transient absorption spectra: 1. the spectrum of the triplet state of the benzidine chromophore formed upon photolysis of A–S–B; 2. the spectrum of the radical cation of the benzidine chromophore formed upon photolysis of N–S–B in the presence of 0.05 M piperylene; 3. the spectrum observed upon photolysis of N–S–B. All the spectra were obtained in cyclohexane 0.5 μ s after the laser pulse.

Thus, intramolecular triplet energy transfer from the benzidine group to the norbornadiene group in N–S–B is thermodynamically possible. On the other hand, calculation from eq 1 reveals that electron transfer from the triplet excited state of the benzidine moiety to the norbornadiene group in N–S–B in cyclohexane is endothermic by 14–16 kcal/mol. Thus, we conclude that in cyclohexane only triplet energy transfer is responsible for the triplet quenching of the benzidine group in N–S–B.

Laser Flash Photolysis Evidence for Singlet Electron Transfer and Triplet Energy Transfer in N–S–B. The evidence for long-distance intramolecular singlet electron transfer and triplet energy transfer in N–S–B based on fluorescence and phosphorescence efficiencies as well as energetic consideration is further strengthened by flash photolysis study. Pulsed laser photolysis of A–S–B in degassed cyclohexane by using 308 nm excitation light gives a strong transient absorption spectrum in the region of 370–480 nm as shown in Figure 2, curve 1. This absorption is assignable to the lowest triplet state²³ of the benzidine chromophore (A–S–³B*), by reference to the transient absorption of the triplet state of *N,N,N',N'*-tetramethylbenzidine.²⁴ Furthermore, this absorption is readily quenched by 1,3-pentadiene or O₂. Pulsed laser photolysis of N–S–B under identical condition leads to absorption of the radical cation and the triplet state of the benzidine chromophore (Figure 2, curve 3). The spectra of these two species overlap extensively in the spectral region of 350–480 nm. However, they can be separated by employing 1,3-pentadiene as a specific triplet quencher. At concentration of the diene in the order of 0.05 M, the lifetime of the triplet state

of the benzidine chromophore is decreased sufficiently (15 ns) to allow monitoring of the radical cation absorbance at times close to the laser pulse. This absorbance was observed in the region of 350–430 nm (Figure 2, curve 2). Analysis of the transient spectra for N–S–B at 350 nm, where the absorption is due to the radical cation, as a function of time reveals that the benzidine radical cation absorption is mainly generated in the time scale of the laser pulse duration. By reference to the fluorescence quenching mentioned in the second section, it is clear that this benzidine radical cation is originated from long-distance singlet electron transfer from the benzidine chromophore to the norbornadiene group.

As shown in Figure 2, the absorption for N–S–B at 450 nm is exclusively due to the triplet state of the benzidine chromophore. Analysis of the transient spectrum for N–S–B at 450 nm as a function of time yields a lifetime of the triplet state of ca. 1.25 μ s. Similarly, the triplet lifetime of the benzidine chromophore in the model compound A–S–B was determined to be 3.60 μ s. Obviously, the triplet state of the benzidine group in N–S–B is quenched by the norbornadiene group. By reference to the phosphorescence efficiency and energetic consideration mentioned in the above section, the triplet quenching of the benzidine group in N–S–B is evidently due to intramolecular triplet energy transfer. By comparison of the triplet lifetime of the benzidine chromophore in N–S–B with that in A–S–B, the efficiency (ϕ_{TT}) and rate constant (k_{TT}) for the intramolecular triplet energy transfer were calculated to be ca. 0.65 and 5.2×10^5 s⁻¹, respectively. This quenching efficiency is close to that obtained by phosphorescence study (ca. 60%), and the value of k_{TT} is comparable to that of the intramolecular triplet energy transfer in the norbornadiene–steroid–benzophenone system.^{17b} To obtain the quantum yield (Φ_{TT})²⁵ of the triplet norbornadiene formation via triplet energy transfer in N–S–B, the quantum yield of the intersystem crossing (Φ_{isc}) from the singlet excited state (N–S–¹B*) to the triplet state (N–S–³B*) is required. By using the perylene isomerization method²⁶ we determined the Φ_{isc} for N–S–B to be 0.56 (see Table 1 and the footnote). Thus, Φ_{TT} is a product of Φ_{ISC} and ϕ_{TT} and is equal to ca. 0.36.

Photosensitized Isomerization of the Norbornadiene to Quadricyclane Group in N–S–B. The photosensitized valence isomerization of norbornadiene to quadricyclane has been the subject of intense experimental and theoretical investigation in view of its significance in solar energy storage²⁷ and mechanistic interests.^{19,20,28} The isomerization mechanism involving triplet–triplet energy transfer has been well understood.¹⁹ Furthermore, dimethyl bicyclo[2.2.1]hepta-2,5-diene-

2,3-dicarboxylate is a good electron acceptor and can also undergo isomerization in the presence of an electron donor sensitizer.²⁰ Based on the observation of chemical induced dynamic nuclear polarization (CIDNP) effects, it has been proposed that this photosensitized isomerization involves electron transfer from the sensitizer to the norbornadiene to generate the singlet state radical-ion pair, intersystem crossing of the resultant singlet radical-ion pair to its triplet state, and recombination of the triplet radical-ion pair to give the triplet norbornadiene followed by rearrangement to the quadricyclane. For molecular N–S–B, the energy of the radical-ion pair, N^{•-}–S–B^{•+}, in cyclohexane was calculated according to eq 1 to be 77–79 kcal/mol. This energy lies above the triplet energy of the norbornadiene group (ca. 53 kcal/mol). Thus, we infer that the triplet radical-ion pair ³(N^{•-}–S–B^{•+}) may undergo recombination to generate the triplet norbornadiene group ³N*–S–B. Therefore, the isomerization of the norbornadiene group in N–S–B might proceed both via triplet–triplet energy transfer and via radical-ion pair recombination mechanisms.

Photoirradiation with $\lambda > 300$ nm of a 2.5×10^{-5} M degassed solution of N–S–B in cyclohexane at room temperature results in valence isomerization of the norbornadiene group to quadricyclane group (Q–S–B) as shown in Chart 1. Under this condition only the benzidine chromophore absorbs the light. Thus, the isomerization of the norbornadiene to quadricyclane group must be attributed to the sensitization via triplet energy transfer and/or electron transfer. The yield of the isomerization product is 100% on the basis of the consumption of the starting material. The assignment of the product as the quadricyclane derivative relies mainly on its ¹H NMR spectrum, which is in close agreement with that reported in the literature. Measurements of product formation at different concentrations revealed that the isomerization is induced by intramolecular photosensitization. The quantum yield of this intramolecular photosensitized isomerization was measured to be ca. 0.07. According to Scheme 1, this quantum yield should be a product of the quantum yield for the formation of the triplet state norbornadiene group resulted both from triplet energy transfer and radical-ion pair recombination and the efficiency of the isomerization reaction from the norbornadiene triplet state (ϕ_{ISO}). In the previous work^{17b} we determined ϕ_{ISO} to be ca. 0.185. This in turn gives the quantum yield for the formation of the triplet norbornadiene in N–S–B to be ca. 0.38. This value is slightly greater than the quantum yield of the norbornadiene triplet formation via triplet energy transfer ($\Phi_{TT} =$ ca. 0.36) given in the above section. Thus, formation of the norbornadiene triplet state via recombination of the triplet radical-ion pair should operate, and the quantum yield of the triplet norbornadiene formation via this process is ca. 0.02.

Formation of triplet state of the norbornadiene chromophore via recombination of the triplet radical-ion pair was supported by the determination of the quantum yield for the isomerization of the norbornadiene group in N–S–B in the presence of *trans*-piperylene. The triplet state energy of *trans*-piperylene is ca. 59 kcal/mol,²⁹ which lies below the triplet state benzidine (63 kcal/mol) but above the triplet norbornadiene group (53 kcal/mol). Thus, *trans*-piperylene may selectively quench triplet benzidine in the presence of triplet norbornadiene. Therefore, the intramolecular photosensitized isomerization of the norbornadiene group in N–S–B in the presence of sufficient amount of *trans*-piperylene should exclusively originate from the singlet electron transfer path. Under this condition the quantum yield

(23) It has been documented that photolysis of *N,N,N',N'*-tetramethylbenzidine in degassed acetonitrile leads to absorptions due to the triplet state and the cation of this compound. For A–S–B, we used a nonpolar solvent (cyclohexane) and only observed the absorption of the triplet state. Indeed, in acetonitrile cation absorption was detected. Analysis of the cation absorption in acetonitrile as a function of laser intensity reveals that the cation is formed via monophotonic excitation of A–S–B to its singlet excited state followed by spontaneous ejection of an electron.

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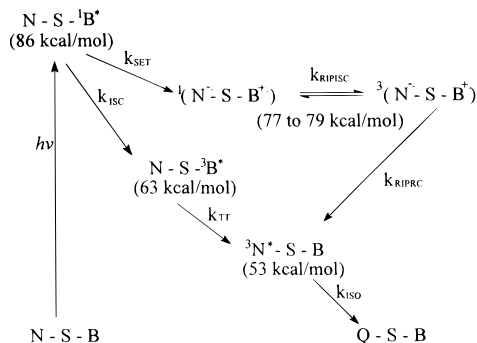
(25) We use the terms “quantum yield” and “efficiency” in the conventional definition. The quantum yield of formation of a given species is based on photons absorbed by the system. The efficiency of formation of a given species from a given state is based on the given state. See: Turro, N. *J. Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; P243.

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Scheme 1^a

^a The data in parentheses represent the energies of the corresponding states relative to the ground state. The energy of the radical ion pair was obtained by calculation from eq 1, and the energies of $N-S-^1B^*$ and $N-S-^3B^*$ were determined by fluorescence and phosphorescence spectra, respectively. The energy of $^3N^*-S-B$ is from ref 20a. $\phi_{SET} = 0.12$, $\phi_{ISC} = 0.56$, $\phi_{TT} = 0.65$, $\phi_{RIPISC} \cdot \phi_{RIPRC} = 0.17$, $\phi_{ISO} = 0.185$, $k_{SET} = 1.1 \times 10^7 \text{ s}^{-1}$, $k_{ISC} = 5.2 \times 10^7 \text{ s}^{-1}$, $k_{TT} = 5.2 \times 10^5 \text{ s}^{-1}$.

for the photosensitized isomerization was determined to be 0.004. By using ϕ_{ISO} (ca. 0.185) the quantum yield of the triplet norbornadiene formation via the singlet electron transfer path is calculated to be 0.02. This value is consistent with that obtained by the quantum yield of triplet norbornadiene formation in the absence of a triplet quencher subtracting Φ_{TT} .

The quantum yield of the triplet norbornadiene formation via the singlet electron transfer pathway (0.02) is a product of Φ_{SET} , the efficiency of the intersystem crossing (ϕ_{RIPISC}) from $^1(N^*-S-B^{*+})$ to $^3(N^*-S-B^{*+})$ and the efficiency of the recombination of the resultant $^3(N^*-S-B^{*+})$ (ϕ_{RIPRC}). Since Φ_{SET} (0.12) is known, $\phi_{RIPISC} \cdot \phi_{RIPRC}$, the efficiency of the triplet norbornadiene formation from $^1(N^*-S-B^{*+})$ via intersystem crossing and the subsequent recombination is calculated to be ca. 0.17.

Mechanism of the Long-Distance Electron Transfer and Triplet Energy Transfer in N-S-B. Scheme 1 outlines the photophysical and photochemical processes which occurred in N-S-B. These involve one long-distance triplet energy transfer process and two long-distance electron transfer processes (the electron transfers from the singlet benzidine and the recombination of the radical-ion pair). It is normally expected that electron transfer and triplet energy transfer will become very inefficient as the donor–acceptor distance increases beyond 5–10 Å. In this study the benzidine and norbornadiene chromophores are separated by 10σ bonds. As mentioned above, calculation revealed that among the various conformation of N-S-B, the extended conformation has the lowest energy. In this conformation the edge-to-edge distance between the norbornadiene and the benzidine groups, defined as the distance between the 3β -O and 17β -N atoms, is ca. 10.8 Å, and the center-to-center distance, defined as the separation between the C-2 in norbornadiene and the center of the *Ph-Ph* bond in benzidine, is ca. 17.0 Å. At such separation between the chromophores electron transfer and triplet energy transfer via a through-space process would be very inefficient. By reference to the precedent works of the long-distance through-bond electron transfer^{3–12} and energy transfer,^{13–17} we infer that through-bond mechanisms operate in the intramolecular electron transfer and triplet energy transfer in N-S-B.

Conclusions

Photochemical reaction and flash photolysis studies revealed that long-distance intramolecular triplet energy transfer and singlet electron transfer from the benzidine to the norbornadiene chromophores occur in N-S-B. Scheme 1 summarizes the

photophysical and photochemical processes in N-S-B. The efficiencies of the various processes shown in this scheme may involve large error, since the uncertainty introduced in one measurement is accumulated in the successive calculations. Nevertheless, regardless of the exact numbers of these efficiencies, this work demonstrated that the valence isomerization of the norbornadiene to the quadricyclane group in N-S-B is induced by long-distance intramolecular triplet photosensitization and by radical-ion pair recombination mechanism. It is evident that the triplet state norbornadiene group is generated by the following two paths: (1) The singlet excited state benzidine chromophore undergoes intersystem crossing with the quantum yield of ca. 0.56 to its triplet state followed by triplet–triplet energy transfer to yield the triplet norbornadiene group with efficiency of ca. 0.65 and the rate constant of ca. $5.2 \times 10^5 \text{ s}^{-1}$. Thus, the quantum yield of the triplet norbornadiene formed via these processes amounts to ca. 0.36. (2) The singlet excited state of the benzidine undergoes electron transfer to the norbornadiene to give singlet radical-ion pair $^1(N^*-S-B^{*+})$ with the quantum yield of 0.12. The resultant $^1(N^*-S-B^{*+})$ intersystem crosses to $^3(N^*-S-B^{*+})$ followed by recombination to generate the triplet norbornadiene group with the efficiency of ca. 0.17. The quantum yield of the triplet norbornadiene generated via this path is only ca. 0.02. The total quantum yield of the triplet formation of the norbornadiene group via the above two paths amounts to ca. 0.38. The long-distance intramolecular electron transfer and triplet energy transfer in N-S-B are believed to proceed via a through-bond mechanism.

Experimental Section

Material. Unless otherwise noted, materials were purchased from Beijing Chemical Work and were used without further purification. Spectral-grade cyclohexane, 2-methyltetrahydrofuran, and acetonitrile were used for absorption and emission spectra, flash photolysis, redox potential measurements, and steady-state photoirradiation measurements. HO-S-17 β -B, HO-S-17 α -B, and N-S-B were synthesized and identified by elemental analysis, IR, MS, and ¹H NMR spectroscopies (see Supporting Information).

Instrumentation. ¹H NMR spectra were recorded at 300 MHz with a Brock spectrometer. MS spectra were run on a VG ZAB spectrometer. UV spectra were measured with a Hitachi UV-340 spectrometer. IR spectra were run on a Perkin-Elmer 983 spectrometer. Steady-state emission spectra were recorded either on a Hitachi EM850 or a Hitachi MPF-4 spectrofluorimeter. Fluorescence lifetime was determined on a Horiba NBES-1100 single photon counting instrument. HPLC was performed on a Varian VISTA 5500 liquid chromatograph with a Lichrosorb RP 18 column.

Fluorescence and Phosphorescence Measurements. Fluorescence was measured in degassed cyclohexane at room temperature. Phosphorescence studies were performed in 2-methyltetrahydrofuran at 77 K, and the sample solutions were degassed by at least three freeze–pump–thaw cycles at a pressure of 5×10^{-5} Torr. The excitation wavelength both for fluorescence and phosphorescence spectra was 300 nm. For comparison of the emission efficiency of N-S-B with A-S-B, the spectra were run using solutions with identical optical density at the excitation wavelength. The relative emission efficiencies were measured from the peak areas of the emission spectra. The fluorescence quantum yields of the benzidine groups in A-S-B and N-S-B were determined in cyclohexane relative to quinine bisulfate in 1 N sulfuric acid.³⁰ The intersystem crossing quantum yield of the benzidine group in N-S-B was determined in cyclohexane by using the piperylene isomerization method relative to benzophenone as a sensitizer of known intersystem crossing yield.²⁶

Redox Potentials of BP and NBD. The redox potentials of A-S-B and MNBD were determined by cyclic voltammetry in acetonitrile,

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using a glassy carbon working electrode and an Ag/AgCl/KCl (saturated) reference electrode in the presence of 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

Laser Flash Photolysis. The laser flash photolysis system has been described elsewhere.³¹ The pump light source was an XeCl excimer laser (Lumonics 500, 308 nm, 10 ns). The probe light source was a xenon arc lamp (Ushio, UXL-500-0). The probe light transmitting through the sample cell was fed to a detection system which consists of a monochromator (Ritsu, MC-10L), photomultiplier (Hamamatsu, R928), digital oscilloscope (Tektronix, 2440) and microcomputer. The decay curve was analyzed by using nonlinear least-squares fitting.

Photoirradiation and Product Analysis. Photoirradiation was carried out in a Pyrex reactor, and the samples were purged with nitrogen. A 450-W Hanovia high-pressure mercury lamp was used as the excitation source. After irradiation the solvent was evaporated from the samples under reduced pressure. The product was separated from the starting material by preparative thin-layer chromatography and characterized by ¹H NMR and mass spectrometers (see Supporting Information). Product yields were determined by analysis of the ¹H NMR spectra and by HPLC analysis. Quantum yields for intramolecular photosensitization isomerization of the norbornadiene group in N-S-B was determined by using a benzophenone/benzohydrol system as the actinometry ($\Phi = 0.74$ in benzene).³²

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Supporting Information Available: Synthesis procedures and data of melting points, elemental analysis, mass spectroscopies, infrared spectroscopies, and ¹H NMR of 3 β -hydroxyandrost-5-en-17 β -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (HO-S-17 β -B), 3 β -hydroxyandrost-5-en-17 α -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (HO-S-17 α -B), 3 β -((2-(methoxycarbonyl)bicyclo[2.2.1]hepta-2,5-diene-3-yl)carboxy)androst-5-en-17 β -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (N-S-B) and 3 β -((2-(methoxycarbonyl)quadriclane-3-yl)carboxy)androst-5-en-17 β -yl-2,2',6,6',N,N',N'-heptamethylbenzidine (Q-S-B) (3 pages). See any current masthead page for ordering and Internet access instructions.

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