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Chemoselective Photorearrangements of Diazinobarrelenes. Deuterium Labeling Study

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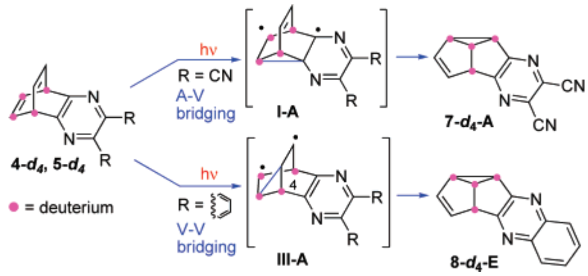

Chemoselective photorearrangements of pyrazino-, quinoxalino-, and benzoquinoxalinobarrelenes were investigated by deuterium-labeling experiment. Photolysis of pyrazinobarrelene **4** and quinoxalinobarrelene **5** with 300 nm region light under either direct or sensitized conditions afforded semibullvalenes **7** and **8**, respectively; benzoquinoxalinobarrelene **6** was inert to both reaction conditions. Irradiation of deuterated pyrazinobarrelene **4-d_4** and quinoxalinobarrelene **5-d_4** afforded deuterated semibullvalenes **7-d_4-A−7-d_4-F** and **8-d_4-A−8-d_4-F**, respectively. Of the two a priori possibilities of bridging, the deuterium-labeling experiment has shown that deuterated pyrazinobarrelene **4-d_4** afforded 98% (C_6D_6) and 95% (CD_3CN) of semibullvalenes generated through aryl−vinyl (A−V) bridging, whereas the quinoxalinobarrelene **5-d_4** furnished 79% (C_6D_6) and 71% (CD_3CN) of semibullvalenes generated through vinyl−vinyl (V−V) bridging. The contrasting photochemical behavior of heteroarene-fused barrelenes **4−6** was explained qualitatively in terms of triplet energy minimization and relative stability of diradicaloid intermediates.

Introduction

Bicyclo[2.2.2]octa-2,5,7-triene (**1**),[1] also named barrelene[1a] because of its concentric π-orbital orientation (Figure 1),[1b] is one of the most fascinating bridged-ring systems in photochemical reactions.[1c,e,f] Forty years ago, Zimmerman and Grunewald[2] reported a most intriguing photochemical behavior of **1** which has led to extensive investigations of several barrelene derivatives[3] and other structural frameworks[4] that contain the required chromophoric groups for di-π-methane (DPM) rearrangement.[5]

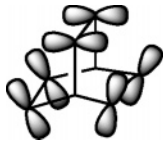

FIGURE 1. Molecular orbital representation of barrelene.

The initial investigations by Zimmerman et al. on barrelene **1** had shown that the direct photolysis of **1** (full arc, quartz

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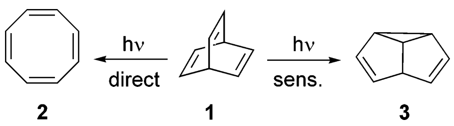
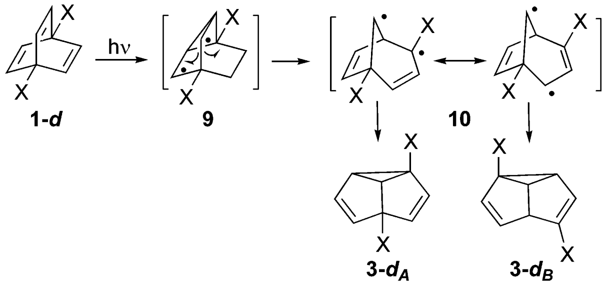
SCHEME 1. Photorearrangement of Barrelene 1

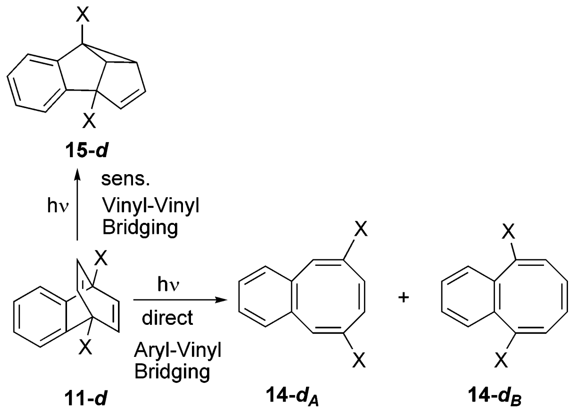


SCHEME 2. Photorearrangement of Deuterated Barrelene 1-*d*



X = hydrogen, deuterium elsewhere

SCHEME 3. Photorearrangement of Deuterated Benzobarrelene 11-*d*



X = hydrogen; deuterium elsewhere

tube, methylcyclohexane solution, room temperature) affords cyclooctatetraene **2**, as supported by IR, NMR, and VPC analyses (Scheme 1).[2] The reaction was perceived to occur initially via intramolecular [2 + 2]-cycloaddition of the excited singlet state of barrelene. On the other hand, the acetone-sensitized reaction gives semibullvalene **3**.

Zimmerman considered two reaction pathways for the sensitized irradiation of barrelene **1**. The first mechanism involved the participation of the three vinylic moieties during the bridging process, and the second involved a stepwise bridging of the two vinylic moieties.[6] They elegantly resolved the problem of discriminating these two mechanisms by substituting all the vinylic protons with deuterium atoms and then determined the distribution of hydrogen in the deuterated products by ^{1}H NMR and mass spectral analyses. A good correlation was noticed between the calculated hydrogen distributions and the experimentally determined values, thus supporting the second mechanism which was thought to involve stepwise bridging of the two vinylic moieties to generate the triplet diradical **9** followed by cyclopropyl carbon fission to afford the symmetrical allylic diradicals **10** (Scheme 2). Closing of the diradicals **10** gives semibullvalenes **3-*d*$_{\mathbf{A}}$** and **3-*d*$_{\mathbf{B}}$**. The considered mechanism was supported by the independent generation of biradicals **10** using azo precursor[7] and through theoretical studies.[8] The mechanism of barrelene rearrangement has become the basis for other workers to predict the pathways of other rearrangement processes.[9,10]

The deuterium-labeling technique was also employed by Zimmerman et al. in predicting the chemoselective photorearrangements of homoarene-fused barrelenes, such as benzobarrelene,[11] naphthobarrelene,[12] and anthrabarrelene.[13] Compared with barrelene **1**, these barrelene analogues can exhibit two types of bridging modes, vinyl−vinyl (V−V) and aryl−vinyl (A−V) bridgings. As shown in Scheme 3, the direct irradiation of deuterated benzobarrelene **11-*d*** affords cyclooctatetraenes **14-*d*$_{\mathbf{A}}$** (major) and **14-*d*$_{\mathbf{B}}$** (minor) derived from A−V bridging, whereas the sensitized reaction gives semibullvalene **15-*d*** generated from the V−V bridging mode (Scheme 3).[11]

The observed chemoselectivity of **11-*d*** under sensitized reaction conditions was rationalized by considering the energy of the triplet state during the initial mode of bridging. Thus, they hypothesized that if the benzene moiety in **11-*d*** was fused with another aromatic ring, bridging would probably occur between the aryl and the vinyl groups as polycyclic aromatic groups are expected to have lower triplet energies than ethylene. This prompted them to study the photochemical behavior of deuterated naphthobarrelene **12-*d*** and anthrabarrelene **13-*d*.** Surprisingly, these two barrelenes underwent V−V bridging (Scheme 4). In both reaction conditions (direct and sensitized), **12-*d*** afforded the DPM photoproduct **16-*d***. However, anthrabarrelene **13-*d*** afforded semibullvalene **17-*d*** under direct

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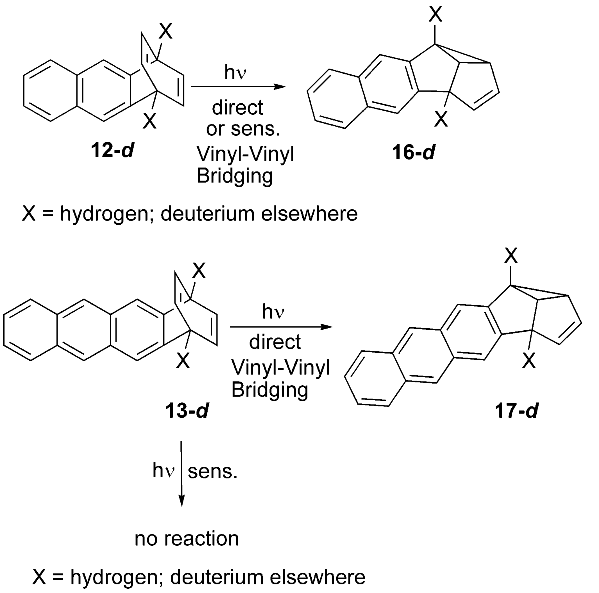
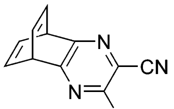
SCHEME 4. Photorearrangement of Deuterated Anthrabarrelene 12-*d* and 13-*d*



irradiation, but no photoproduct was observed in the sensitized reaction conditions.[12,13] One interesting aspect about the photochemistry of arene-fused barrelenes is the preference for V−V bridging despite a priori possibilities for A−V bridging.

Encouraged by these impressive mechanistic explorations of barrelene and homoarene-fused barrelenes[6,7,11] by Zimmerman and his co-workers, we decided to embark on the photochemical investigation of heteroarene-fused barrelenes **4**−**6** to find out if similarities and differences exist among these barrelene systems in terms of chemoselectivity as compared to that of the homoarene-fused systems and also to ascertain if the same type of rearrangement will occur as in the case of barrelene **1**.

In principle, the rearrangement products of the title compounds can be accessed by two types of bridging interaction, A-V and V−V bridging modes. The deuterium-labeling technique has provided us the opportunity to identify the primary bridging mode under direct and sensitized reaction conditions. We report herein the syntheses and photorearrangements of diazinobarrelenes **4**−**6**.



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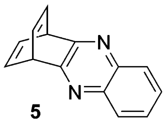

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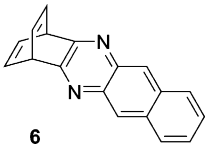

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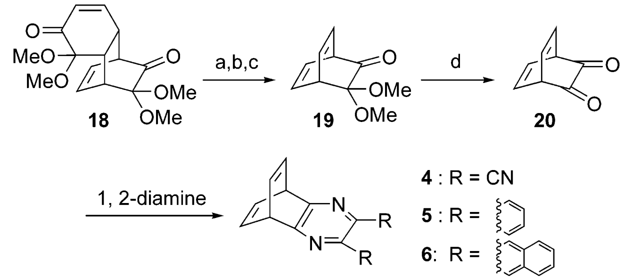
Results

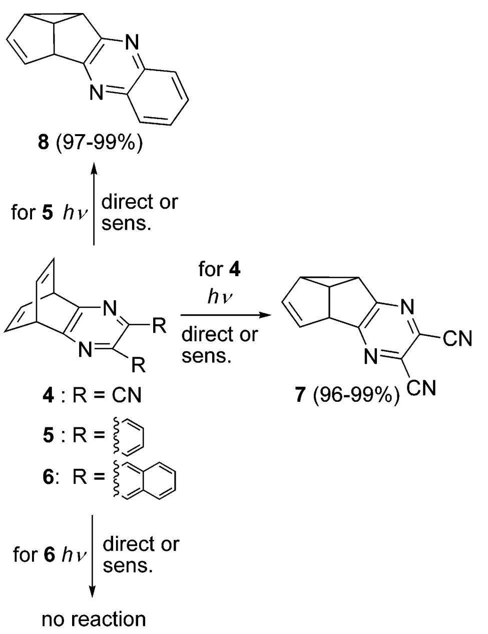
Synthesis of Heteroarene-Fused Barrelenes 4−6. Bicyclic dienedione **20** was synthesized using masked *o*-benzoquinone (MOB) dimer **18** as the starting material. Employing the method developed in our laboratory.[14,15] Followed by condensations with the corresponding 1,2-diamine, heteroarene-fused barrelenes could be synthesized facilely (Scheme 5). Detailed experimental procedures for **19**,[14] **20**,[15] **4**−**8**, and deuterated compounds **19-*d*$_4$**, **20-*d*$_4$**, **4-*d*$_4$**, and **5-*d*$_4$** along with spectral data assignment are available in Supporting Information.

SCHEME 5. Synthesis of Heteroarene-Fused Barrelenes[a]



[a] Reaction conditions: (a) 220 °C, phenyl vinylsulfide; (b) *m*CPBA, −78 °C; (c) Et$_3$N, 130 °C, sealed tube (70% over 3 steps); (d) H$_2$SO$_4$, 65 °C (84%).

SCHEME 6. Photolysis of Heteroarene-Fused Barrelenes 4, 5, and 6



Photolysis of Heteroarene-Fused Barrelenes 4−6. Irradiation of pyrazinobarrelene **4** either in benzene, acetonitrile, or acetone solvent afforded semibullvalene **7** in 96−99% yield (Scheme 6). Under similar reaction conditions, quinoxalinobarrelene **5** afforded semibullvalene **8** in near quantitative yield; however, for benzoquinoxalinobarrelene **6**, no characterizable photoproducts were detected; the starting material was recovered after 2 h of irradiation.

The structure of **7** was established as semibullvalene based on spectral analyses (Table 1). The chemical shifts in the ^{1}H NMR spectrum which showed two doublets of doublets at δ 5.65 (J = 2.4, 5.2 Hz, 1H) and δ 5.59 (J = 2.4, 5.2 Hz, 1H) were assigned to the vinylic protons. The chemical shifts at δ 3.28 (dt, J = 2.4, 6.4 Hz, 1H), δ 3.67 (q, J = 6.4 Hz, 1H), and δ 3.31 (t, J = 6.4 Hz, 1H) were assigned to the cyclopropyl protons. The observed multiplicity at δ 3.67 is characteristic of tricyclo[3.3.0.0^{2,8}]octene systems.[16] In the case of quinoxali-

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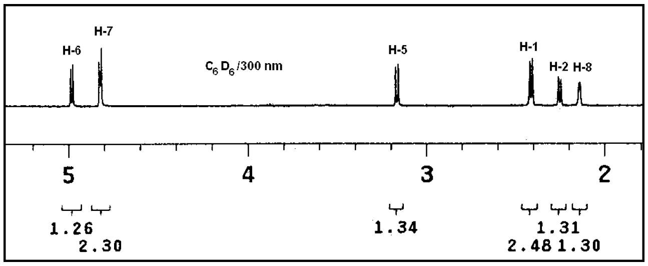


FIGURE 2. ^{1}H NMR (400 MHz) spectrum of tricyclooctene moieties of photoproducts **7-*d*$_4$-A**−**7-*d*$_4$-F**.

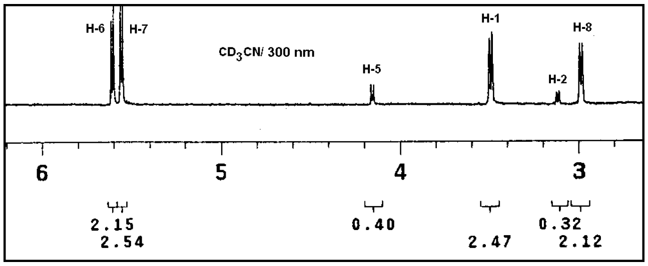
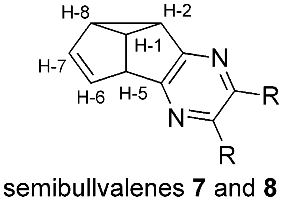


FIGURE 3. ^{1}H NMR spectrum of tricyclooctene moieties of photoproducts **8-*d*$_4$-A**−**8-*d*$_4$-F**.

TABLE 1. Pertinent ^{1}H NMR Data for Nondeuterated Semibullvalenes 7 and 8



	proton chemical shifts in nonaromatic positions (ppm, CDCl$_3$)[a]					
semibullvalene	H-1	H-2	H-5	H-6	H-7	H-8
7	q 3.67	t 3.31	dd 4.16	dd 5.65	dd 5.59	dt 3.28
8	q 3.51	t 3.16	dd 4.22	dd 5.65	dd 5.54	dt 2.98

[a] Starting material in deuterated benzene was degassed for 1 h prior to irradiation with 300 nm region light for 2 h.

nosemibullvalene **8**, the proton spectral features at the fused cyclopentanoid moiety proved almost directly superimposable upon that of pyrazinosemibullvalene **7**.

Photolysis of Deuterated Pyrazinobarrelene 4-*d*$_4$ and Quinoxalinobarrelene 5-*d*$_4$. Photoreactions of **4-*d*$_4$** and **5-*d*$_4$** were monitored by ^{1}H NMR and were stopped when the starting material had disappeared. The ^{1}H NMR spectra in Figures 2 and 3 illustrate the spectral profiles of the tricyclic octene moieties of the deuterated semibullvalenes furnished after irradiating barrelenes **4-*d*$_4$** in perdeuterated benzene and **5-*d*$_4$** in perdeuterated acetonitrile with 300 nm region light. Similar spectral profiles as that of Figure 2 were obtained for the irradiation of **4-*d*$_4$** in perdeuterated acetonitrile; however, overlapping peaks were observed for the vinylic protons at H-6 and H-7. Irradiation of **5-*d*$_4$** in perdeuterated benzene showed spectral profiles similar to Figure 3. One interesting observation of their spectra is the appearance of proton peaks ascribable to all the hydrogens of the tricyclooctene moiety.

Discussion

Multiplicities in the Photochemistry of Heteroarene-Fused Barrelenes. According to the accepted view of DPM photorearrangements of bicyclic systems,[5] photoreactions proceed from the triplet excited states, thus we presume that the same multiplicity is involved in the rearrangements of barrelenes **4** and **5** since similar rearrangements and product distributions were observed in both reaction conditions (direct and sensitized). In addition, the nitrogen-containing aromatic group present in these heterobarrelene systems which can be excited via n,π^* and π,π^* triplet states has greatly influenced the observed multiplicity through spin−orbit interaction.[17] Furthermore, pyrazine ($\phi_{ISC} = 1.0$)[18b] and quinoxaline ($\phi_{ISC} = 0.99$)[17d] moieties, which are presented in these barrelene systems, were shown to have very high intersystem crossing quantum yields relative to their homoarene counterpart.[18] It is important to note that, for benzoquinoxalinobarrelene **6**, no photoproduct was observed in both reaction conditions.

Bridging Mode of Photochemical Rearrangement. It is of considerable interest to identify the pathways taken by barrelenes **4** and **5** during the photochemical event. As shown in Scheme 7, there are five possible semibullvalenes (**7-*d*$_4$-A** ≡ **7-*d*$_4$-E**; **8-*d*$_4$-A** ≡ **8-*d*$_4$-E**) that can be generated from three routes; two of these routes (**I** and **II**) involve A−V bridging, and the other one (route **III**) involves V−V bridging. For the purpose of hydrogen distribution accounting, we label the identical pyrazinosemibullvalenes as **7-*d*$_4$-A** and **7-*d*$_4$-E**, and the quinoxalinobarrelenes as **8-*d*$_4$-A** and **8-*d*$_4$-E**. Route **I** involves primary aryl−vinyl bridging at C3−C4, generating the diradicaloid intermediate **I-A**; breaking of the cyclopropyl moiety generates the secondary diradicaloid intermediates having the canonical structures **I-B$_1$** and **I-B$_2$**. Ring closure on both sides of the allylic radicals gives the photoproducts **7-*d*$_4$-A** and **7-*d*$_4$-B** or **8-*d*$_4$-A** and **8-*d*$_4$-B**. In the case of route **II**, initial A−V bridging at C3−C5 gives rise to intermediates **II-A**; further rearrangement generates intermediates of canonical structures **II-B$_1$** and **II-B$_2$** which ultimately furnish semibullvalenes **7-*d*$_4$-C** and **7-*d*$_4$-D** or **8-*d*$_4$-C** and **8-*d*$_4$-D**. Finally, route **III** commences through V−V bridging at C5−C4 to generate the diradicaloid intermediate **III-A**. Breaking of the cyclopropyl ring of **III-A** at the C5−C8 bond affords intermediate **III-B** which upon closing of the diradical furnishes **7-*d*$_4$-E** or **8-*d*$_4$-E**. Bond fission at C4−C8 in **III-A** affords intermediate **III-C**, and closure of this diradical furnishes the semibullvalene **7-*d*$_4$-F** or **8-*d*$_4$-F**.

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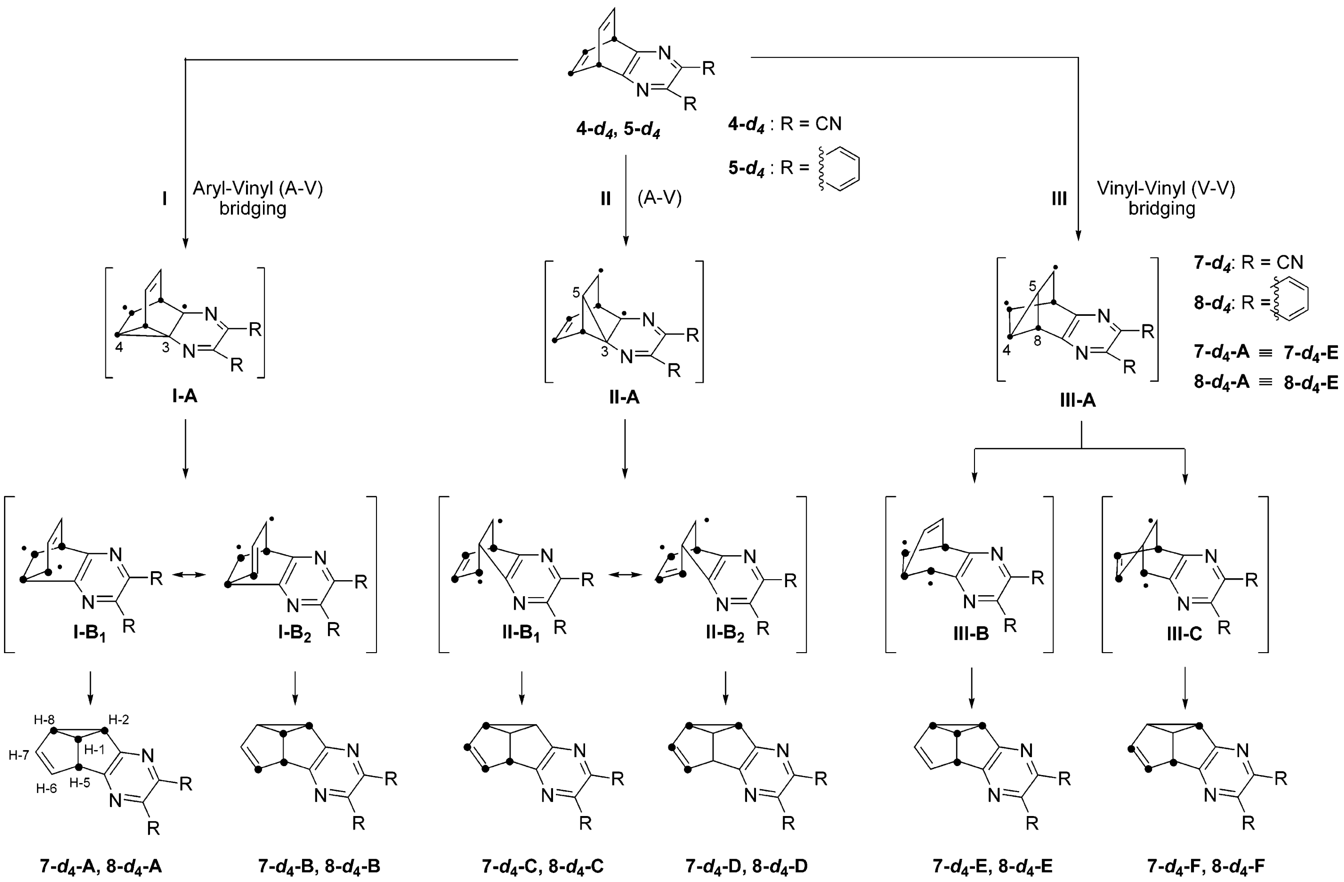
SCHEME 7. Conceivable Bridging Modes and Photoproducts of 4-d_4 and 5-d_4



Perusal of the spectral profiles of photoproducts (Figures 2 and 3, vide supra) suggests that a number of semibullvalenes were produced from **4-d_4** and **5-d_4**. This deduction is based on the following observations: (1) proton peaks appear in all the nonaromatic positions of the photoproducts; and (2) from the mass spectral analysis (see Experimental Section) of the starting materials, only 6% residual hydrogen was observed at the deuterated sites; however, as depicted in the spectral profiles of **7-d_4** and **8-d_4**, the amount of hydrogen in most carbons of the nonaromatic moiety of the photoproducts is relatively high. For instance, the lowest proton intensity (H-2, 1.31) for the photoproducts of **4-d_4** in benzene (Figure 2, vide supra) when integrated relative to the other proton peaks is about 13.1% H, which is way above the 6% residual hydrogen of the deuterated sites.

A question arises as to which and what ratio of the photoproducts in Scheme 7 could account for the observed hydrogen distributions that are depicted in Figures 2 and 3. To solve this problem, first, we determined the theoretical hydrogen distribution of each semibullvalene. Considering the 6% residual hydrogen from the deuterated sites and the two protons from the nondeuterated sites of the photoproducts, each semibullvalene will have a total of 2.06 H. Neglecting secondary isotope effect, each deuterated carbon of semibullvalene will have 0.015 H, whereas the nondeuterated carbon will have 1.0 H. The result of this calculation is summarized in Table 2. Theoretically, the distribution of hydrogen at the nonaromatic moiety of pyrazinosemibullvalenes **7-d_4-A**−**7-d_4-F** and **8-d_4-A**−**8-d_4-F** should be the same.

Next, we normalized the observed hydrogen distributions in the photoproducts **7-d_4** and **8-d_4** to 2.06 to account for the residual hydrogen (see Supporting Information). These are summarized in Tables 3 and 4. As shown in these tables, the observed hydrogen distributions for the photoproducts **7-d_4** and **8-d_4** in the two solvents are very close, suggesting that there is no profound effect of solvent on the observed hydrogen distribution. If we correlate the observed hydrogen distributions with that of the calculated values of the individual semibullvalene in Table 1, one would notice a very poor correlation.

TABLE 2. Calculated Hydrogen Distributions in Semibullvalenes 7-d_4-A−7-d_4-F and 8-d_4-A−8-d_4-F

	calculated hydrogen distributions[a]					
semibullvalene	H-1	H-2	H-5	H-6	H-7	H-8
7-d_4-A or **8-d_4-A**	0.015	0.015	0.015	1.00	1.00	0.015
7-d_4-B or **8-d_4-B**	0.015	0.015	0.015	0.015	1.00	1.00
7-d_4-C or **8-d_4-C**	1.00	1.00	0.015	0.015	0.015	0.015
7-d_4-D or **8-d_4-D**	1.00	0.015	1.00	0.015	0.015	0.015
7-d_4-E or **8-d_4-E**	0.015	0.015	0.015	1.00	1.00	0.015
7-d_4-F or **8-d_4-F**	1.00	0.015	0.015	0.015	0.015	1.00

[a] Calculated hydrogen distributions were normalized to 2.06 H to account for the 6% residual hydrogen as determined by mass spectral analysis.

TABLE 3. Observed Hydrogen Distributions in Photoproducts of 4-d_4

	hydrogen distributions in photoproducts of **4-d_4**[a]					
solvent	H-1	H-2	H-5	H-6	H-7	H-8
C_6D_6	0.511	0.270	0.276	0.260	0.474	0.268
CD_3CN	0.531	0.268	0.268	0.260	0.472	0.262

[a] Hydrogen distributions calculated from ^{1}H NMR integrations (400 MHz) were normalized to 2.06 H to account for the residual hydrogen as determined by mass spectral analysis.

TABLE 4. Observed Hydrogen Distributions in Photoproducts of 5-*d*$_4$

solvent	H-1	H-2	H-5	H-6	H-7	H-8
	Hydrogen distributions in photoproducts of **5-*d*$_4$**[a]					
C_6D_6	0.490	0.076	0.082	0.457	0.494	0.459
CD_3CN	0.509	0.066	0.082	0.443	0.523	0.437

[a] Hydrogen distributions calculated from ^{1}H NMR integrations (400 MHz) were normalized to 2.06 H to account for the residual hydrogen as determined by mass spectral analysis.

TABLE 5. Bridging Modes and Yields of Semibullvalenes 7-*d*$_4$-A−7-*d*$_4$-F and 8-*d*$_4$-A−8-*d*$_4$-F under Direct Irradiation

semibullvalene (bridging Mode)[a,b]	yield[c] (%) C_6D_6	yield[c] (%) CD_3CN
7-*d*$_4$-A (A−V)[b]	21.1 (23.2)	21.5 (22.3)
7-*d*$_4$-B (A−V)	21.7 (23.8)	21.5 (22.3)
7-*d*$_4$-C (A−V)	22.9 (25.2)	24.4 (25.4)
7-*d*$_4$-D (A−V)	23.5 (25.8)	24.4 (25.4)
7-*d*$_4$-E (V−V)[b]	0.8 (0.9)	2.1 (2.2)
7-*d*$_4$-F (V−V)	1.0 (1.1)	2.3 (2.4)
8-*d*$_4$-A (A−V)	3.4 (3.5)	6.5 (6.2)
8-*d*$_4$-B (A−V)	3.7 (3.8)	8.1 (7.7)
8-*d*$_4$-C (A−V)	6.2 (6.4)	6.9 (6.5)
8-*d*$_4$-D (A−V)	6.8 (7.0)	8.5 (8.1)
8-*d*$_4$-E (V−V)	41.5 (42.9)	38.7 (36.8)
8-*d*$_4$-F (V−V)	35.2 (36.4)	36.5 (34.7)

[a] A−V = aryl−vinyl bridging. [b] V−V = vinyl−vinyl bridging. [c] Yields were calculated based on the relative ratios of the proton intensities of the deuterated products. The yields in parentheses indicate normalization to 100%. See Supporting Information for the detailed calculations.

TABLE 6. Total Yields of Photoproducts Derived from A−V and V−V Bridging Modes

reactant (solvent)	total yield[a] (%) Σ(A−V)[b]	total yield[a] (%) Σ(V−V)[c]	ratio Σ(A−V):Σ(V−V)
4-*d*$_4$ (C_6D_6)	89.2 (98.0)	1.8 (2.0)	50:1
4-*d*$_4$ (CD_3CN)	91.8 (95.4)	4.4 (4.6)	21:1
5-*d*$_4$ (C_6D_6)	20.1 (20.7)	76.7 (79.3)	0.26:1
5-*d*$_4$ (CD_3CN)	30.0 (28.5)	75.2 (71.5)	0.4:1

[a] Yields in parentheses indicate normalization to 100%. [b] Sum of photoproducts derived from A−V bridging. [c] Sum of photoproducts derived from V−V bridging.

This suggests that several semibullvalenes were generated from **4-*d*$_4$**. The proton peak observed at H-1, for example, is therefore a contribution of all the possible semibullvalenes presented in Scheme 7 (vide supra). A linear combination of the component contributions was found which fit the observed distribution (see Supporting Information). The results of the calculations are presented in Table 5.

From Table 5, one can easily notice the dominant A−V bridging mode of **4-*d*$_4$** and the V−V bridging preference of **5-*d*$_4$**. The bridging preference of pyrazinobarrelene **4-*d*$_4$** is opposite to that of benzobarrelene[11] and 2,3-naphthobarrelene;[12] however, the quinoxalinobarrelene bridging mode is in agreement with the bridging pattern of several barrelene derivatives,[3] including the above-mentioned barrelenes. The proximity of the product distributions to a 1:1 ratio for the different pairs of photoproducts such as **7-*d*$_4$-A** and **7*d*$_4$-B** and **7-*d*$_4$-C** and **7-*d*$_4$-D** is a good indication for the absence of an appreciable secondary isotope effect.[6]

In Table 6, we present a summary of the yields of photoproducts derived from the different bridging modes. For the photoproducts of **4-*d*$_4$** in the two solvents, the relative yields derived from A−V bridging are 89 and 92%, whereas the yields derived from V−V bridging are 2 and 4%. In contrast to that of **4-*d*$_4$**, the relative yields for the photoproducts of **5-*d*$_4$** derived from A−V bridging are 20 and 30%, whereas the yields derived from V−V bridging are 77 and 75%. Notably, we encountered a significant experimental error for the values obtained from **5-*d*$_4$** in deuterated acetone. This may be attributed to the fact that under sensitized conditions the photoproducts may also absorb energy within the wavelength region of the sensitizer. Nevertheless, the A−V/V−V ratios of the photoproducts clearly show the contrasting bridging preferences of barrelenes **4-*d*$_4$** and **5-*d*$_4$**.

Factors Controlling the Rearrangement. Two striking results can be noticed regarding the photochemical behavior of barrelenes **4**−**6**: First, the observation that only semibullvalenes were furnished in both reaction conditions (direct and sensitized) in the cases of **4** and **5** and the insensitivity of **6** to photochemical reaction, and second, the contrasting bridging mode of the two barrelenes as construed from the deuterium-labeling experiment.

In the first case, successful sensitization demonstrates intervention of a triplet reactant, which is in accord with the rearrangements of several aromatic barrelene derivatives;[3,11,16] however, we also obtained the same photoproducts with similar product distributions under direct irradiation. As discussed previously, this kind of photochemical behavior strongly indicates that singlet−triplet intersystem crossing[19] of **4** and **5** is very efficient.

In the second case, the presence of cyano groups in **4** has effected the preferential aryl−vinyl interaction presumably by conjugative stabilization of the diradical intermediates **IA$_1$**−**IA$_4$**[3,20] as detailed in Scheme 8. This kind of radical stabilization cannot be observed during the initial V−V bridging (Scheme 7, vide supra) because the radicals are not conjugated to the sp^2 atoms of the aryl moiety. The strong directional effects of the nitrile groups, which can stabilize diradicaloid intermediates, have enhanced the localization of the triplet energy on this part of the molecule.[21]

The V−V bridging preference of quinoxalinobarrelene **5** is striking. With the triplet energy of the aromatic moiety (T_1 quinoxaline = 60.6 kcal/mol)[22b] relatively lower than the triplet energy of ethylene (T_1 ethylene = 82.1 kcal/mol),[22a,c] we expect an initial A−V bonding interaction. To explain this bridging mode, an alternative consideration would be the triplet energy of the π-systems during the initial bridging process. Qualitatively, we can predict the energy of the reaction course by employing Zimmerman's bridging hypothesis.[11,16e] Primary V−V bridging of **5** leads to a structure that can be approximated

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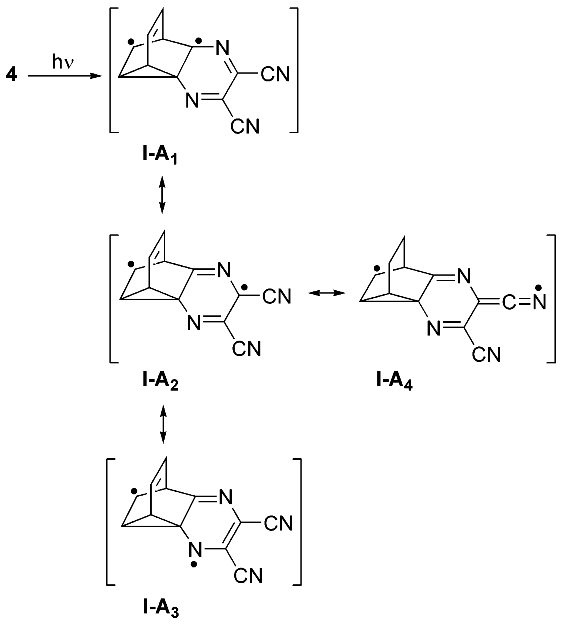
SCHEME 8. Resonance Structures of Barrelene 4 Generated through Initial A−V Bridging



electronically by a cisoid butadiene of which cyclohexadiene (T_1 = 53.5 kcal/mol)[22d] is an appropriate model. In the case of the quinoxaline moiety, initial bonding with the vinyl group gives rise to a vinylquinoxaline structure. The triplet energy of the resulting vinylquinoxaline moiety can be approximated from the triplet energies of napththalene (T_1 = 60.9 kcal/mol),[22b] vinylnaphthalene (T_1 = 60.0 kcal/mol),[22b] and quinoxaline (T_1 = 60.6 kcal/mol).[22a] The attachment of the vinyl group in naphthalene decreases its triplet energy by about one unit. Assuming that quinoxaline exhibits the same photochemical behavior as naphthalene (their triplet energies are comparable), then vinylquinoxaline will have a T_1 energy of about 59 kcal/mol, which is way above the triplet energy of the cisoid butadiene. In effect, the excitation energy will be more heavily inclined toward the vinyl group similar to that of naphthobarrelene.[12] If we apply this kind of analysis to pyrazinobarrelene **4**, the dicyanopyrazinovinyl moiety generated through initial A−V bridging will have a T_1 energy of about 43 kcal/mol, which can be deduced from the triplet energies of benzene (T_1 = 84.3 kcal/mol),[22b,e] styrene (T_1 = 61.7 kcal/mol),[22b,e] pyrazine (T_1 = 76.6 kcal/mol),[22b] and dicyanobenzene (T_1 = 72.7 kcal/mol).[22b] This triplet energy (43 kcal/mol) is lower than the triplet energy of cisoid butadiene, thus A−V bridging is preferred. The bridging preference of **4** is in contrast to that of benzobarrelene which favors V−V bridging. A−V bridging in benzobarrelene will give rise to a homostyrene structure whose triplet energy is higher than the cisoid butadiene; thus V−V bridging is observed.[11,16]

Unlike that of homoarene-fused anthrabarrelene,[13] which gives DPM product during direct irradiation, but is inert under sensitized reaction, the benzoquinoxalinobarrelene **6** is insensitive to both reaction conditions. The photochemical behavior of anthrabarrelene is explained in terms of the participation of the T_2 state. In the case of benzoquinoxalinobarrelene **6**, the excitation energy, which is expected to be minimal, is insufficient to overcome the energy barrier during the initial bridging due to the aromatic stability of the benzoquinoxalinobarrelene moiety.[12] Hence, energy minimization for the perturbed triplet state is one factor that has to be considered in predicting the chemoselectivity and photoreactivity of heteroarene-fused barrelenes.

Conclusion

In the course of our investigation on photochemical studies of heteroarene-fused barrelenes **4**−**6**, we noticed that pyrazinobarrelene **4** preferentially underwent A−V bridging, whereas quinoxalinobarrelene **5** favored V−V bridging. Benzoquinoxalinobarrelene **6** was unreactive to both photochemical reaction conditions. The results clearly demonstrate that heteroarene-fused barrelenes follow the general mechanism of di-π-methane rearrangement. The A−V bridging preference of pyrazinobarrelene **4** and the V−V bridging preference of quinoxalinobarrelene **5**, which are predicted quantitatively through deuterium-labeling experiment and qualitatively through Zimmerman's initial bridging hypothesis and stability of diradicaloid intermediates, suggest that electronic effects and energy minimization of triplet excited states during the initial bridging modes are important factors in determining the chemoselectivity of the process. The inertness of benzoquinoxalinobarrelene **6** is attributed to the minimal excitation energy present in this molecule. Likewise, similarities and differences between the homoarene-fused barrelenes[11−13] and heteroarene-fused barrelenes **4**−**6** with regards to the bridging modes can be rationalized in terms of energy minimization of triplet states. Finally, the close correlation between the calculated and observed hydrogen distributions of the photoproducts further supports the stepwise mechanism of di-π-methane rearrangement.

Experimental Section

3,3-Dimethoxybicyclo[2.2.2]octa-5,7-dien-2-one (19). To a reaction tube were added 1 equiv of MOB dimer **18**[14a] and 4 equiv of phenyl vinylsulfide in toluene (20 mL) and degassed under liquid nitrogen for 1 h before sealing. The solution was heated in an oven at 220 °C for 4 h. After removing the solvent under reduced pressure, the crude bicyclic sulfide was purified by a silica gel column (ethyl acetate/hexanes, 1:6). To a solution of the sulfide in dichloromethane, stirred in a dry ice bath, was gradually added a solution of *m*CPBA (1 equiv in CH_2Cl_2). The resulting mixture was heated to room temperature and then quenched with $NaHCO_3$; the sulfoxide crude product was extracted with CH_2Cl_2 and the solvent removed in vacuo. The crude product in ethyl acetate and triethylamine (catalytic) was placed in a reaction tube, degassed before sealing, and heated at 130 °C for 3 h; then the solvent was stripped off under reduced pressure, and the final product was purified by column chromatography (ethyl acetate/hexanes, 1:10) to obtain a light yellow liquid **19** in 70% yield.

Bicyclo[2.2.2]octa-5,7-diene-2,3-dione (20). To a dark-colored reaction flask was added compound **19** (1.80 g, 10 mmol) in 2 N H_2SO_4 (250 mL), heated at 65 °C, and stirred for 3 h. The reaction mixture was extracted with ether; then the organic layer was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by a silica gel column (ethyl acetate/hexanes, 1:2) to obtain a yellow crystalline substance **20** in 84% yield.

3,6-Diazatricyclo[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene-4,5-dicarbonitrile (4). Compound **20** (200 mg, 1.5 mmol) in MeOH (15 mL) was mixed with diaminomaleonitrile (**21**) (178 mg, 1.65 mmol) and heated at 50 °C for 8 h. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column (ethyl acetate/hexanes, 1:1) and yielded upon recrystallization from CH_2Cl_2 or ethyl acetate a white crystalline substance **4** (mp 183.7−184.1 °C) in 80% yield.

3,10-Diazatetracyclo[10.2.2.0^{2,11}0^{4,9}]hexadeca-2(11),3,5,7,9,13,15-heptaene (5). Following the procedure described for **4**, condensation of compound **20** (200 mg, 1.5 mmol) with diaminobenzene (**22**, 178 mg, 1.65 mmol) afforded a white crystalline substance **5** (mp 144.0−144.6 °C) in 95% yield: IR (neat): $\bar{\nu} = 3076, 2980, 1575, 1355, 1300, 1101, 902, 770, 754, 602\ cm^{-1}$; UV/vis (MeOH) λ_{max} (ϵ) = 333 (8500), 317 (9600), 251 (14000), 239 (13000); ^{1}H NMR (400 MHz, $CDCl_3$; 25 °C) δ = 4.97−5.01 (m, 2H; CH), 6.95−6.98 (m, 4H; ═CH), 7.58−7.62 (m, 2H; aromatic), 7.82−7.86 (m, 2H; aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 49.5, 128.1, 128.6, 137.6, 137.8, 157.9; MS (EI, 75 eV) *m/z* (%) 207 (100) [$M^+ + H$], 206 (18), 182 (5), 181 (22), 154 (8), 136 (7), 77 (6); HRMS (EI) calcd for $C_{14}H_{10}N_2$ [M^+] 206.0844; found 206.0841. Anal. Calcd (%) for $C_{14}H_{10}N_2$ (206.08): C, 81.53; H, 4.89; N, 13.58. Found: C, 81.48; H, 5.62; N, 12.80.

3,14-Diazapentacyclo[14.2.2.0^{2,15}0^{4,13}0^{6,11}]icosa-2,4,6(11),7,9,12,14,17,19-nonaene (6). Compound **20** (200 mg, 1.5 mmol) in MeOH was mixed with naphthalenediamine (**23**, 261 mg, 1.65 mmol) and heated under reflux for 12 h. Following the workup procedure for **4**, compound **6** (mp 204.2−204.7 °C) was obtained in moderate yield (44%).

1,2,5,6,7,8,11,12-Octadeutero-3,3,10,10-tetramethoxytricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (18-*d*$_8$). To a reaction bottle containing D_2O (16 g, 18 mmol) was added $SOCl_2$ (10 mL) dropwise. The SO_2 formed during the reaction was removed by bubbling nitrogen gas before adding guaiacol (**24**, 5 g, 40 mmol), then the solution was heated to reflux for 3 days. The crude product was extracted with ether and concentrated under reduced pressure. This was done in two runs before cooling (ice bath) the deuterated phenol **24-*d*$_4$**, which was dissolved in MeOH. Diacetoxyiodobenzene (DAIB) (14.2 g, 44 mmol) was gradually added while stirring, and after 20 min, the ice bath was removed and the product was monitored by TLC. After removing the solvent using a rotary evaporator, the crude product was quenched with Na_2CO_3 (aq) and extracted with ethyl acetate. The organic layer was washed with water and brine solution, dried ($MgSO_4$), and concentrated under reduced pressure to obtain a gray-colored powder which can be recrystallized from ethyl acetate into a white powder, **18-*d*$_8$** (6 g, 96%) (mp 172.5−174.0 °C). Percentage deuteration of the MOB dimer **18-*d*$_8$** was determined by LRMS which showed *m*/*e* peaks at 314, 315, and 316 with relative intensities of 0.3, 0.15, and 1, respectively.

Calculations for Percent Deuterium in Dimer 18-*d*$_8$. Deuterated dimer **18-*d*$_8$** was made as the reference compound for approximating the deuterium content of the photoreactants **4-*d*$_4$** and **5-*d*$_4$**. The reason being that, in the mass spectra of nondeuterated barrelenes **4** and **5**, we observed [$M^+ + H$] *m/z* peaks, so there was a problem of calculating the deuterium content of the deuterated barrelenes. Our assumption of using **18-*d*$_8$** as the reference compound is reasonable; the deuterated sites in the dimer were exactly located in the same position when we analyzed the ^{1}H NMR spectra of the deuterated barrelenes **4-*d*$_4$** and **5-*d*$_4$**. For example, in **4-*d*$_4$**, the ^{1}H NMR chemical shift at δ 7.01 was observed which can be integrated to 2 H, suggesting that the protons in one of the two vinylic moieties and the bridgehead protons were deuterated. From LRMS analysis of **18-*d*$_8$**, the mass spectrum consisted of a series of peaks with major contributions from masses 314, 315, and 316; the normalized mass intensities were 29.61, 15.89, and 100, respectively. The *m/z* values of 314, 315, and 316 correspond to dimers having six, seven, and eight deuteriums, respectively. From the relative intensities of these *m/z* values, we obtained about 94% deuteration of **18-*d*$_8$** with the following contributions from the various masses: *m/z* 314, 15.26%; *m/z* 315, 9.56%; *m/z* 316, 68.73%. Contributions from *m/z* values with four and five deuterium were considered negligible so they were not included in the computation. Percent deuterium of **18-*d*$_8$** was computed as follows:

Assuming we have 100 molecules for each *m/z* value, then *m/z* of 314 will have 29.61 × 6 D and 29.61 × 2H; *m/z* of 315 will have 15.89 × 7 D and 15.89 × 1 H; *m/z* of 316 will have 100 × 8 D and 100 × 0 H; therefore, contributions from various masses will be *m/z* 314; %D = 177.66 D/1164 × 100 = 15.26%; *m/z* 315, %D = 111.23 D/1164 × 100 = 9.56%; *m/z* 316, %D = 800 D/1164 × 100 = 68.73%.

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Supporting Information Available: Experimental procedures and characterization data for new compounds not reported in the Experimental Section, copies of ^{1}H, ^{13}C NMR, and UV absorption spectra for new compounds, and detailed sample calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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