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Substituent effects on the bridging modes of photochemical rearrangements of pyrazino-, quinoxalino-, and benzoquinoxalinobarrelenes

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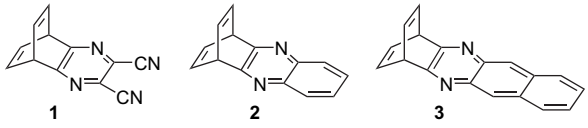
ABSTRACT

Chemoselective photorearrangements of symmetrically substituted pyrazinobarrelene **4**, quinoxalinobarrelene **5**, and benzoquinoxalinobarrelenes **6** and **7** containing polar and non-polar groups under various conditions are described. In both direct and sensitized irradiation conditions, barrelenes **4**–**7** afforded similar bridging modes and photoproduct distributions suggesting a resemblance in the multiplicities of photoreactants upon excitation. Irradiation of pyrazinobarrelene **4a** furnished almost equal amounts of photoproducts derived from DPM (vinyl–vinyl bridging) and ADPM (aryl–vinyl bridging) pathways. Pyrazinobarrelenes **4b**–**d** underwent chemoselective rearrangements via the ADPM route. In the case of quinoxalinobarrelenes **5a**–**c** and benzoquinoxalinobarrelenes **6b**,**c**, vinyl–vinyl bridging was strongly favored. Benzoquinoxalinobarrelene **6a** was insensitive to photochemical reactions. Heteroaryl–vinyl bonding was the preferred primary interaction in benzoquinoxalinobarrelene **7a** whereas **7b** favored the DPM route via vinyl–vinyl bridging. The photochemical behavior of the title compounds was explained in terms of energy minimization of the perturbed triplet state and diradical stabilization by polar and non-polar substituents. Plausible mechanisms for the photochemical reactions are also described.

1. Introduction

Barrelene and its derivatives have been proven to be excellent substrates for photochemical studies. They undergo facile photoisomerizations to the corresponding cyclooctatetraenes through a singlet-state mediated pathway or semibullvalenes (SBs) through a triplet-state mediated pathway based on the irradiation conditions employed.[1] There has been considerable interest in recent years to evaluate the factors that are responsible for the observed chemoselectivity in the phototransformation of barrelenes to semibullvalenes. For several years, Zimmerman et al. have explored the photochemical behaviors of several arene-fused barrelenes,[2] and the group has observed that structural features and minimization of triplet energies greatly influence the selective transformations of these bicyclic systems. Several substituted barrelenes have been explored by Scheffer,[3] Bender,[4] Hemetsberger,[5] George,[6] and others,[7] and the results of the investigations suggest that steric and electronic effects are major factors in controlling the observed selectivity of product formation.



1 2 3

In previous work, we carried out photorearrangements of several heteroarene-fused barrelenes such as pyrazino-, quinoxalino-, and benzoquinoxalino-fused barrelenes under direct or sensitized conditions and investigated how structures and substituents affect the bridging preferences of these nitrogen-containing barrelene systems. Unlike arene-fused barrelenes, which have gained considerable attention by photochemists, less work has been devoted to heteroarene-fused barrelenes apparently due to their lack of easy accessibility. Previously, we have reported our partial results[1a,8] on these bicyclic systems, to our knowledge, only two examples of the photorearrangement of heteroarene-fused barrelenes had been reported in the literature.[9]

Recently, we published our work[10] on the photorearrangement of unsubstituted heteroarene-fused barrelenes **1**, **2**,[9b] and **3**. Through deuterium labeling experiment, we noticed that aryl–vinyl (A–V) bridging or aza-di-π-methane[11] (ADPM) route was the primary mode of bridging for pyrazinobarrelene **1** and vinyl–vinyl (V–V) bridging or di-π-methane[1,12] (DPM) route was the bridging preference for quinoxalinobarrelene **2** under either direct or

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sensitized conditions; benzoquinoxalinobarrelene **3** was insensitive in both conditions. To address the issue on the effects of substituents during the course of rearrangement, we introduced polar and non-polar substituents at the strategic sites of the barrelenes. The substituents were introduced in such a way that molecular symmetry was maintained and possible modes of the rearrangement could be distinguished. Herein, we report our complete investigations on the photochemical reactions of symmetrically substituted pyrazinobarrelene **4**, quinoxalinobarrelene **5**, and benzoquinoxalinobarrelenes **6** and **7**.

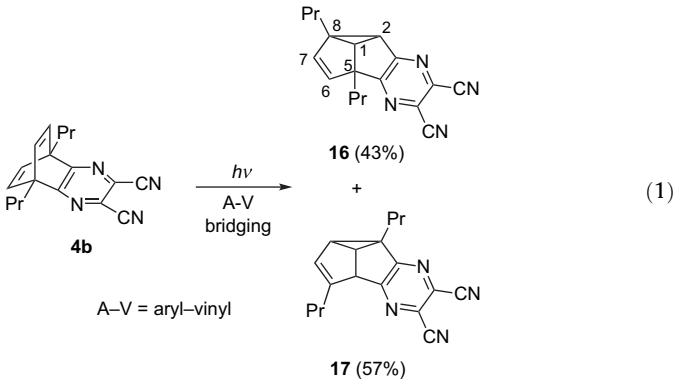
2. Results and discussion

2.1. Synthesis of photoreactants

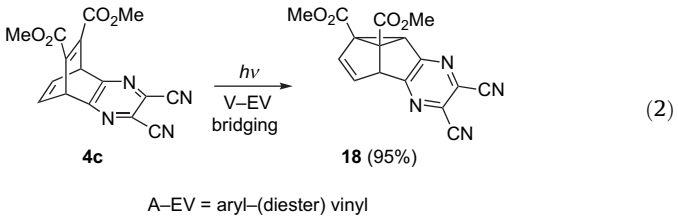
Bicyclic α-diketones **8a**,**c** were prepared as described in the literature.[8e,13] Diketone **8b** was prepared in a two-step process; first, by reducing the carbonyl group of bicyclicketo ester **38**[14] with $NaBH_4$ at 0 °C and then subsequently deprotecting the ketal with HCl followed by oxidation with *o*-iodoxybenzoic acid (IBX) at reflux condition to generate the diketone in 60% yield (Scheme 1). Pyrazinobarrelenes **4a**–**d** were prepared as shown in Scheme 2. Pyrazinobarrelene **4a**[8e] was prepared by means of biscondensation reaction of α-diketone **8a** with ethylenediamine **9** under acid-catalyzed condition to furnish dihydropyrazinobarrelene **49**; further oxidation of **49** was found to be difficult, although a number of attempts with different oxidants and conditions were tried, highest yield of this oxidation was observed by using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene, affording the final product **4a** in 16% yield. Pyrazinobarrelene **4b**[8e] was easily accessed in good yield from the condensation reaction of **8a** in ethanol with **10** under acid condition. Treatment of α-diketone **8b** with **10** at 50 °C in MeOH and then monitoring the completeness of reaction by NMR afforded pyrazinobarrelene **4c** in 80% yield. Diketone **8c** in ethanol was treated with 2,3-diaminomaleonitrile **10** under acid-catalyzed condition at 75 °C for 15 h to produce the pyrazinobarrelene **4d**[1a] in 85% yield. Quinoxalinobarrelenes **5a**–**c** and benzo[*g*]quinoxalinobarrelenes **6a**–**c** were obtained in good yields following similar procedure[1a] (Scheme 3). The dibenzo[*f*,*h*]quinoxalinobarrelenes **7a** and **7b** (vide infra) were synthesized as described in our earlier communication (Fig. 1).[8b]

2.2. Photochemical reactions

The result of direct irradiations in benzene and acetone-sensitized reactions of barrelenes **4**–**7** in a Rayonet reactor with light of broad spectrum at 350 nm region are shown in Schemes 4–10 and succinctly summarized in Table 1. With the exception of semibullvalenes (SBs) **18**, **26**, and **29**, whose product distributions were expressed as isolated yields, the percentage yields of the rest of the photoproducts were based on the ^{1}H NMR (400 MHz) integrations of the irradiated mixtures in degassed deuterated solvents. The dipropyl-substituted pyrazinobarrelene **4a** in benzene furnished three isomeric SB photoproducts **13**–**15** in 53:22:25 ratio, respectively (Scheme 4). SB **13** produced via initial vinyl–vinyl (V–V) bridging of **4a** was obtained as the major product whereas SBs **14** and **15** generated via initial ary–vinyl (A–V) bridging were formed in almost equal amounts.



(1)



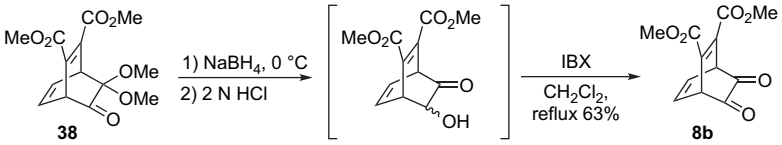
(2)

A–EV = aryl–(diester) vinyl

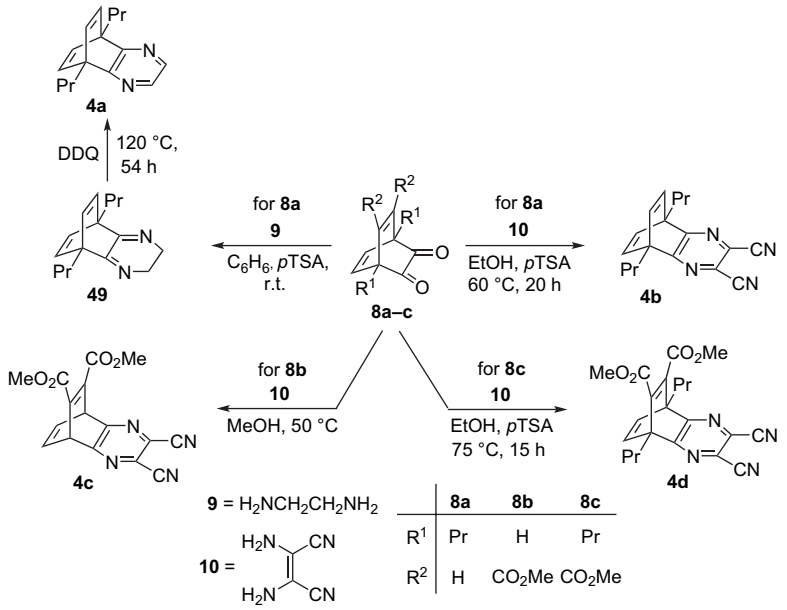
In the case of pyrazinobarrelene **4b**, which has the nitrile functionalities at the pyrazine moiety, the dicyanosemibullvalenes **16** (minor) and **17** (major) were produced via A–V bridging either under direct or sensitized conditions (Eq. 1, Table 1). Pyrazinobarrelene **4c**, which contains nitrile and ester functionalities, furnished semibullvalene **18** in excellent isolated yield either under direct or sensitized reactions. The product was generated by primary vinyl–(diester)vinyl (V–EV) bridging mode (Eq. 2). Irradiation of pyrazinobarrelene **4d** in benzene furnished isomeric SBs **19**–**22**, all arisen from heteroaryl–vinyl bridging (Scheme 5). Similar results were observed under sensitized condition (Table 1, vide supra). The photoproducts **19** and **20** with a combined yield of 56% were furnished via initial A–EV bridging whereas the photoproducts **21** and **22** with a combined yield of 44% were afforded by primary A–V bonding interaction.

Quinoxalinobarrelene **5a** upon irradiation with light at 350 nm region in benzene furnished three regioisomeric SBs **23** generated via V–V bridging as major (71%) and SBs **24** and **25** furnished via A–V bridging as minor (13% and 16%, respectively) photoproducts (Scheme 6). Interestingly, irradiation of **5a** under sensitized conditions produced similar results (Table 1, vide supra). In the case of quinoxalinobarrelenes **5b** and **5c**, which contain the ester functionalities symmetrically attached at the vinylic moieties, only SB photoproducts generated via initial V–EV bridging were obtained (Scheme 7). Irradiation of **5b** in benzene furnished quinoxalinosemibullvalene **26** in excellent isolated yield; **5c** afforded the quinoxalinosemibullvalenes **27** and **28** in 62% and 38%, respectively, based on ^{1}H NMR integrations.

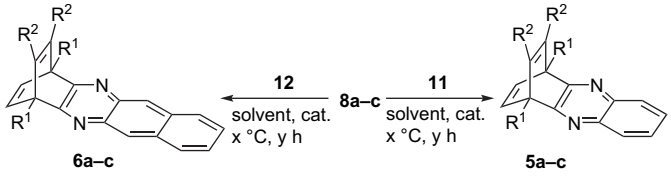
Irradiation of benzo[*g*]quinoxalinobarrelene **6a** either under direct or sensitized conditions afforded no photoproducts; the solutions became darkened and no characterizable photoproduct was



Scheme 1. Synthesis of bicyclic α-diketone **8b**.



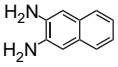
Scheme 2. Syntheses of pyrazinobarrelenes **4a**–**d**.



Compound	amine	solvent	cat.	x°C	y (h)	product (yield,%)
8a	**11**	EtOH	*p*TSA	70	3	**5a** (99)
	12	EtOH	*p*TSA	80	8	**6a** (85)
8b	**11**	MeOH	none	50	---*	**5b** (95)
	12	MeOH	none	reflux	---*	**6b** (48)
8c	**11**	EtOH	*p*TSA	reflux	3	**5c** (94)
	12	EtOH	*p*TSA	reflux	3	**6c** (98)

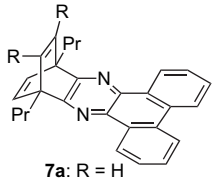
* = reaction monitored until starting material completly consumed.

11 = 

12 = 

a: R^1=Pr; R^2 = H
b: R^1 = H; R^2 = CO_2Me
c: R^1 = Pr; R^2 = CO_2Me

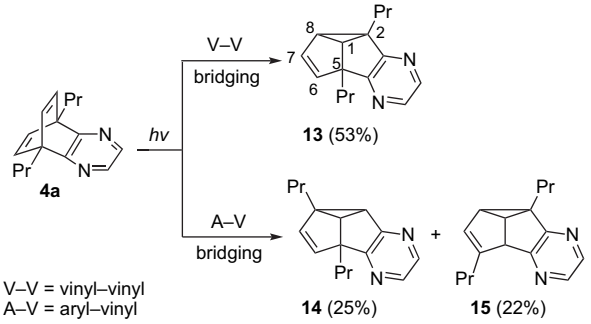
Scheme 3. Syntheses of quinoxalinobarrelenes **5a**–**c** and benzoquinoxalinobarrelenes **6a**–**c**.



7a: R = H
7b: R = CO_2Me

Figure 1. Structures of **7a**,**b**.

obtained after prolonged irradiation (Scheme 8, Table 1). Benzo[*g*]quinoxalinobarrelene **6b**, which contains the ester functionalities, produced SB **29** in good yield; the photoproduct was generated via initial V–EV bridging mode. Barrelene **6c**, which is



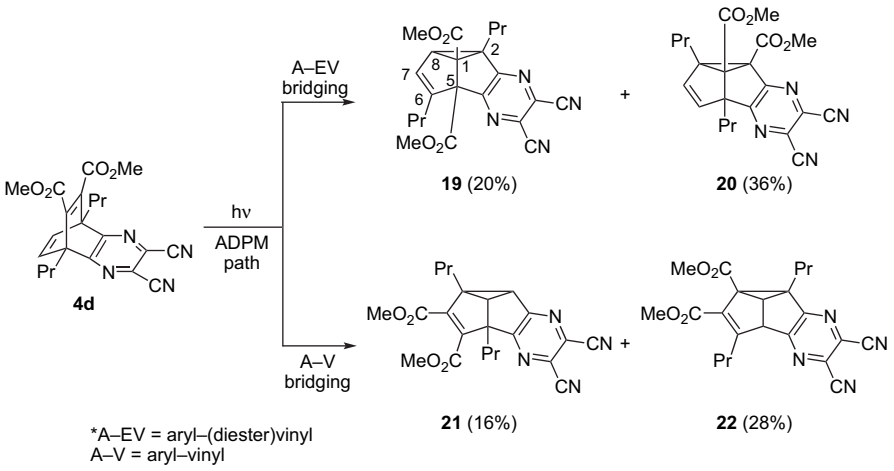
Scheme 4. Photorearrangement of pyrazinobarrelene **4a**.

installed with ester and propyl substituents, afforded SBs **30** and **31** with a product ratio of 59:41 generated via initial V–EV bridging.

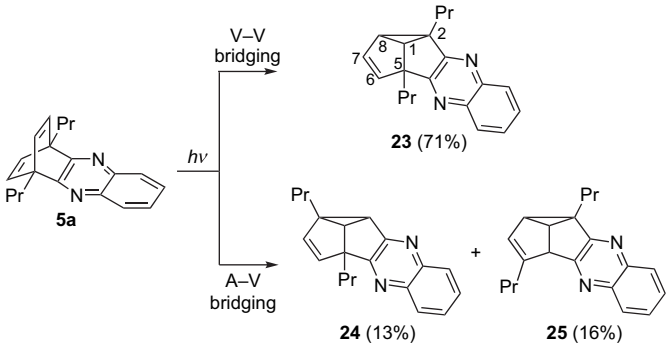
Direct irradiation of dibenzo[*f*,*h*]quinoxalinobarrelene **7a** in benzene led to the formation of three primary SB photoproducts **32**–**34**[8b] in 16:44:40 ratio, respectively (Scheme 9, Table 1). Compound **32**, which resulted from initial V–V bridging was obtained as minor product whereas **33** and **34** resulted from initial A–V bridging were formed in equal amounts. Similar results were obtained when the reaction was performed in acetone. In contrast to the reaction of **7a**, the irradiation of diester-substituted **7b** in benzene proceeded predominantly via V–EV bridging to produce **35** and **36** in 42:38 ratio (Scheme 10), and **37** generated via A–EV bridging in 20% yield.

2.3. Structural elucidation of photoproducts

The structures of the photoproducts were distinguished from their ^{1}H NMR, ^{13}C NMR, and 2D NMR COSY spectral data. The ^{1}H NMR spectra of SBs **13**–**15** showed the typical aromatic proton chemical shifts at δ 7.84–8.06 and the vinyl proton chemical shifts of a tricyclic octene moiety at δ 4.9–5.44; cyclopropyl proton chemical shifts were observed at δ 2.36–2.68. Propyl chemical shifts could easily be detected at δ 0.92–2.36. The three regioisomers could be differentiated by comparing the proton chemical shifts at C-7. SB **13** showed the vinylic and allylic proton coupling constants of 5.0 and 3.0 Hz, respectively, for its C-7 proton centered at δ 5.09



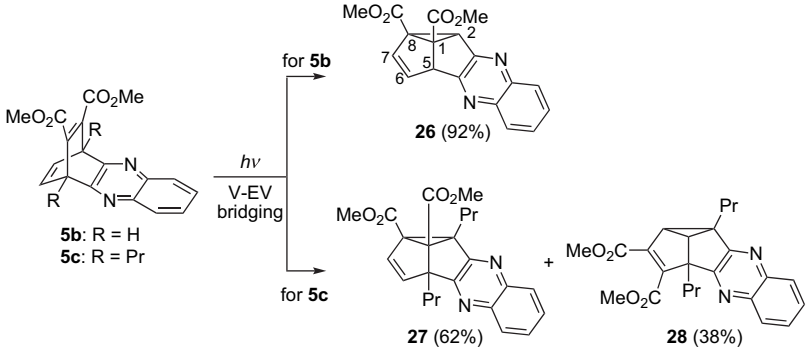
Scheme 5. Photorearrangement of pyrazinobarrelene **4d**.



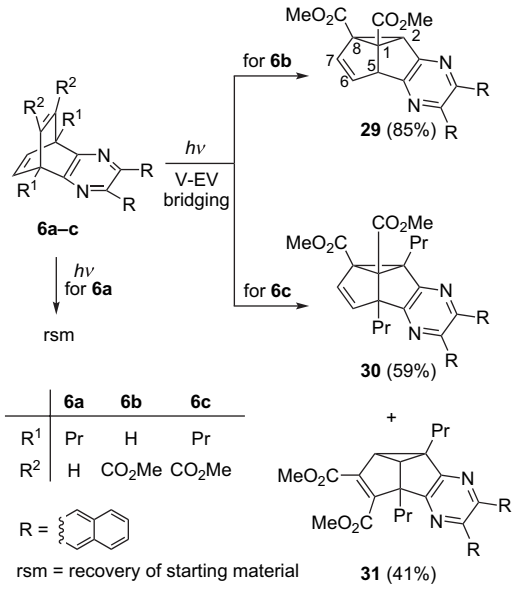
Scheme 6. Photorearrangement of quinoxalinobarrelene **5a**.

(dd, J=5.0, 3.0 Hz, 1H). SB **14** showed only vinylic proton coupling constant of 5.0 Hz for its C-6 and C-7 protons centered at δ 5.08 and 5.44, respectively, suggesting that propyl groups were attached at C-5 and C-8. In the case of **15**, the C-7 proton with a chemical shift of 4.90 ppm (d, J=1.5 Hz, 1H) exhibited a small coupling constant with the allylic proton at C-8; however, no vinylic proton coupling was observed indicating that propyl group was attached at C-6. The structures of SBs **13**–**15** were further elucidated by COSY experiment (see Supplementary data). Except for the aromatic proton resonance signals in **14** and **15**, the spectral profiles of SBs **16** and **17** proved almost superimposable upon that of **14** and **15**, respectively (see Section 4). In the case of SBs **18**–**22**, which contain the nitrile and ester functionalities along with propyl substituents (except **18**), the restricted orientation of the cyclopentyl group is apparent with vinyl carbon resonance signals observed over the range δ 121.0–144.3 and bridgehead carbon resonance signals at δ 46.7–69.4. Methyl ester carbon signals were observed at around 52 ppm whereas the cyanide carbon chemical shifts were discernible at around 113 ppm. Propyl carbon signals were detected over the range δ 13.9–34.4. The ^{1}H NMR of **18** showed the C-2–H as a singlet at δ 4.63 whereas the C-5–H was observed as a doublet at δ 4.73 (d, J=2.8 Hz, 1H). The spin multiplicity of C-5 proton was due to its interaction with the vinylic proton at C-6 whose ^{1}H NMR signal was detected at δ 5.87 (dd, J=2.8, 5.2 Hz, 1H). SBs **19**–**22** could easily be distinguished from the vinylic proton signals. In the case of SB **19**, a single vinylic proton chemical shift, which was assigned to CH-7 (δ=5.31), was observed as doublet with a coupling constant of 1.9 Hz. This small coupling constant is due to its interaction with the adjacent cyclopropyl proton. By contrast, **20** exhibited an AB spin interaction for the two vinylic protons, which have chemical shifts of 5.71 and 5.57 ppm and coupling constant of 5 Hz. SBs **21** and **22** did not exhibit vinylic proton chemical shifts suggesting a full replacement of the C-6 and C-7 protons with substituents but the two SBs could easily be differentiated by their vinylic carbon resonance signals; the ^{13}C NMR chemical shifts at δ 140.2 and 137.3 were assigned to structure **21**, which contains the ester functionalities at the vinylic moiety whereas the vinylic carbon resonance signals at δ 144.3 and 132.9 were assigned to structure **22**, which contains the ester and propyl groups at the vinylic moiety.

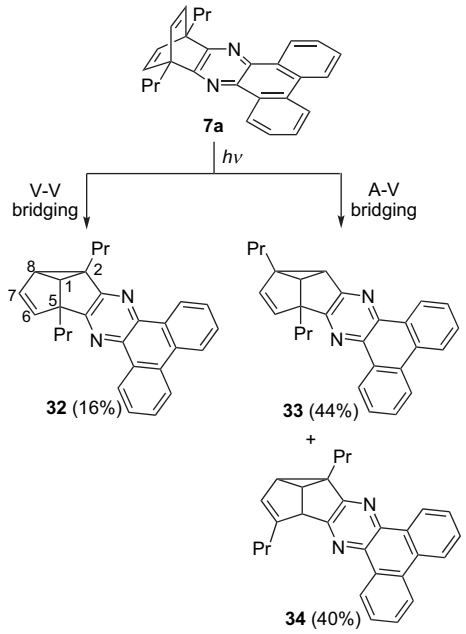
Except for the typical carbon resonance signals of the quinoxaline moiety, which were observed over the range δ 128–155, the spectral profiles of quinoxalinobarrelenes **23**–**25** at the fused cyclopentanoid moieties proved almost directly superimposable



Scheme 7. Photorearrangement of quinoxalinobarrelene **5b**,**c**.

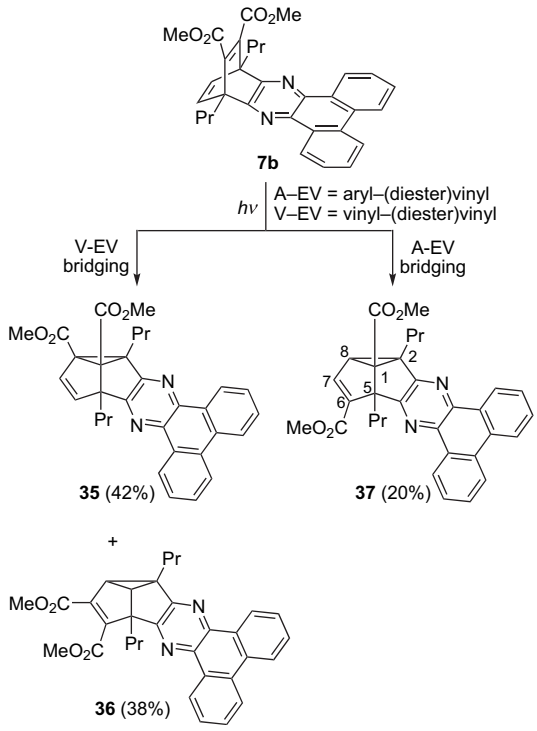


Scheme 8. Photorearrangement of benzoquinoxalinobarrelenes **6a–c**.



Scheme 9. Photorearrangement of dibenzoquinoxalinobarrelene **7a**.

upon that of pyrazinobarrelenes **13–15** (see Section 4). SBs **26–28** showed the quinoxaline proton signals over the range δ 7.2–8.1. Proton signal at δ 4.58, which was observed as a singlet was assigned to cyclopropyl proton of **26** along with the two vinylic protons, which were observed as doublet of doublets at δ 5.64 and 5.88, respectively. The vinylic proton signals at δ 5.63 and 5.40, which appeared as an AB system (AB, J=5.2 Hz, 2H) were assigned to **27**. These signals were not present in **28**, which showed cyclopropyl proton chemical shifts centered at δ 3.32 and 3.11. Propyl and ester spectral profiles of **26–28** were similar to the other barrelene systems discussed earlier. In the case of benzo[*g*]quinoxalinosemibullvalene **29**, the spectral feature was almost similar to that of SB **26**. The spectral profile of SBs **30** and **31** was reminiscent of the spectral features of **27** and **28**. The proton resonance signals of benzo[*f*,*h*]quinoxalinosemibullvalenes **32–34** at the fused



Scheme 10. Photorearrangement of dibenzoquinoxalinobarrelene **7b**.

rings were similar to that of quinoxalinobarrelenes **23–25**, respectively, whereas the SBs **35** and **36** were comparable to that of SBs **27** and **28**, respectively. The structures of **32–34** were further supported by COSY experiment (see Supplementary data). The structure of SB **37** was also established based on spectral analyses. The ^{1}H NMR signal showed a broad peak centered at δ 5.23 and was assigned to the vinylic proton. The proton chemical shifts at δ 3.74 and 3.93 were assigned to the methyl ester moieties whereas the proton signals over the range δ 1.03–2.84 were assigned to the propyl moieties. Aromatic protons of the benzoquinoxalino moieties were detected at δ 7.71–9.36.

2.4. Discussion

*2.4.1. Multiplicities in the photorearrangements of barrelenes **4–7***

It is interesting to note that all the heteroarene-fused barrelenes we investigated undergo either the di-π-methane (DPM) and/or aza-di-π-methane (ADPM) rearrangement when subjected to either direct or sensitized irradiations. According to the current views of DPM photorearrangements of bicyclic systems,[1] the photoreactions proceed from triplet excited states, thus we presume that the same multiplicity is involved in the rearrangements of barrelenes **4–7** since the same rearrangements and product distributions were observed in both direct and sensitized irradiation conditions. Photorearrangements of barrelene analogues **4–7** are in contrast to some of the related barrelene systems of Zimmerman[2d,e,15] and others,[16] which afford [2+2]-cycloaddition photoproducts during direct irradiation. Explanation for such difference could be that nitrogen-containing pyrazine and quinoxaline were known to have very high quantum yields of intersystem crossing relative to their homoarene counterpart[17] and thus could be excited via n, π* and π, π* triplet states[18] to yield DPM and/or ADPM products.

*2.4.2. Bridging modes and photorearrangements of pyrazinobarrelenes **4a–d***

Pyrazinobarrelene **4a** having the propyl substituents at the bridgehead carbons exhibit two possibilities of bridging (vinyl–

Table 1
Bridging modes of symmetrically substituted barrelenes and product ratio of photoproducts under direct and sensitized irradiation conditions

Reactant	Photoproduct (ratio, %)[a]			
	Direct irradiation[b]		Sensitized irradiation[c]	
	V–V[d]	A–V/A–EV[d]	V–V[d]	A–V/A–EV[d]
4a	**13** (53)	**14** (25), **15** (22)	—	—
4b	——	**16** (43), **17** (57)	——	**16** (45), **17** (55)
4c	**18** (95)[e]	——	**18** (98)[e]	——
4d	——	**19** (20), **20** (36), **21** (16), **22** (28)	——	**19** (26), **20** (37), **21** (16), **22** (21)
5a	**23** (71)	**24** (13), **25** (16)	**23** (72)	**24** (6), **25** (22)
5b	**26** (92)[e]	——	**26** (98)[e]	——
5c	**27** (62), **28** (38)	——	**27** (55), **28** (45)	——
6a	Rsm[f]	Rsm[f]	Rsm[f]	Rsm[f]
6b	**29** (85)[e]	——	**29** (86)[e]	——
6c	**30** (59), **31** (41)	——	**30** (50), **31** (50)	——
7a	**32** (16)	**33** (44), **34** (40)	**32** (14)	**33** (43), **34** (43)
7b	**35** (42), **36** (38)	**37** (20)	**35** (47), **36** (40)	**37** (13)

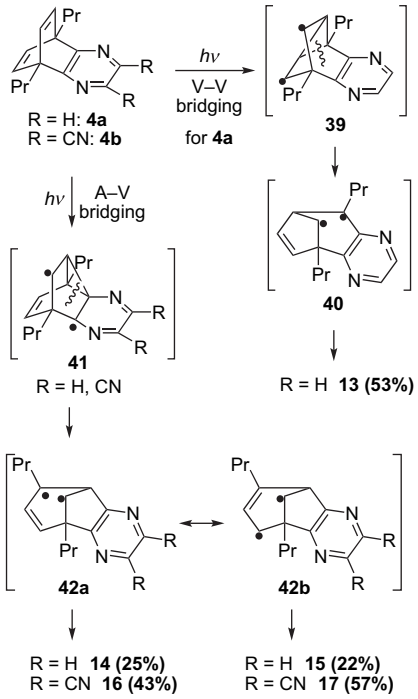
[a] Product ratio of photoproducts obtained from ^{1}H NMR integrations.
[b] Starting materials in benzene were irradiated with 350 nm region light.
[c] Starting materials in acetone were irradiated with 350 nm region light.
[d] A–V/A–EV=aryl–vinyl/aryl–diester vinyl bridging; V–V=vinyl–vinyl bridging; ——=not observed; —=not determined.
[e] Isolated yields.
[f] Recovery of starting material.

vinyl and aryl–vinyl) with almost the same yields of photoproducts (**13** (53%) vs **14** and **15** (47%)). Zimmerman's bridging hypothesis[2d,e,19] can explicably account for the observed primary bridging preferences. Primary vinyl–vinyl (V–V) bonding of **4a** will lead to a structure that can be approximated electronically by a *cisoid* butadiene of which cyclohexadiene (T_1=53.5 kcal/mol)[20a] can be an appropriate model. Aryl–vinyl (A–V) bonding will give rise to a vinylpyrazine structure whose triplet energy (T_1=54 kcal/mol) can be approximated from the triplet energies of benzene (T_1=84.3 kcal/mol),[20b] styrene (T_1=61.7 kcal/mol),[20b,c] and pyrazine (T_1=76.6 kcal/mol).[20b] The approximated value is very close to the *cisoid* butadiene triplet energy. The similar yields of photoproducts derived from the two bridging modes reflect the distribution of triplet energies between the two chromophoric moieties.[21] On the other hand, the bridging preference of **4b** differed to that of pyrazinobarrelene **4a** and generated photoproducts mainly derived from aryl–vinyl (A–V) bridging[10] just like **1**. The efficient site selectivity of **4b** can be attributed to the presence of nitrile moiety, which not only lowers the triplet energy of the aromatic group[16c] but also reduces the driving force (less exothermic) for intramolecular energy transfer to the homodiene moiety.

The observed product distributions from chemoselectivity of **4a** and **4b** can be rationalized by considering a stepwise mechanism as depicted in Scheme 11. Pyrazinosemibullvalene **13** is furnished via intermediates **39** and **40** whereas pyrazinosemibullvalenes **14**–**17** are generated via intermediates **41** and **42a**,**b**. The dominant photoproduct **13** in **4a** whose yield (53%) is slightly higher than the combined yields (47%) of **14** and **15** can be ascribed to the relative stability of intermediates **39** and **41**; the former has the aromatic moiety intact whereas the latter has the aromatic moiety partially disrupted.[3]

In the case of **4b**, which favors the aryl–vinyl bridging mechanism, the generation of **17** as the dominant photoproduct over that of **16** is quite surprising; intermediate **42b**, which generates **17** has a secondary allylic radical whereas **42a**, which generates the minor product **16** has a tertiary allylic radical. The stability of the photoproducts[28] presumably controls the percentage distribution of **16** and **17**. The ADPM rearrangement of **4b** further supports Zimmerman's bridging hypothesis wherein V–V bridging will lead to a *cisoid* butadiene structure with T_1 of 53.5 kcal whereas primary A–V bridging will lead to a structure with T_1 of 43 kcal/mol, which can be deduced from the triplet energies of benzene,[20b] styrene,[20b,c] pyrazine,[20b] and dicyanobenzene[20b], thus, aryl–vinyl bridging is preferred.

The diester-substituted barrelenes **4c** and **4d** also give remarkable site selectivities, with **4c** generating an exclusive DPM photoproduct **18** and with **4d** furnishing ADPM products **19** and **20** via A–EV bridging and **21** and **22** via A–V bridging. This contrasting behavior of **4c** and **4d** in terms of bridging preferences accentuates the directional effect of propyl and ester substituents as regard to the bridging mode. Actually, we expect **4c** to favor the ADPM route with the triplet energy heavily inclined on the aromatic moiety just like **4d**, but ^{1}H NMR analysis of photoproduct **18** clearly reveals the assigned structure. Vinylic proton at C-7 centered at δ 5.72 was observed as doublet (d, J=5.2 Hz, 1H) due to its coupling with the adjacent C-6 proton centered at δ 5.87 (dd, J=2.8, 5.2 Hz, 1H), which is also coupled with the C4–H. The cyclopropyl proton centered at



Scheme 11. Plausible mechanism for the photorearrangement of barrelenes **4a**,**b**.

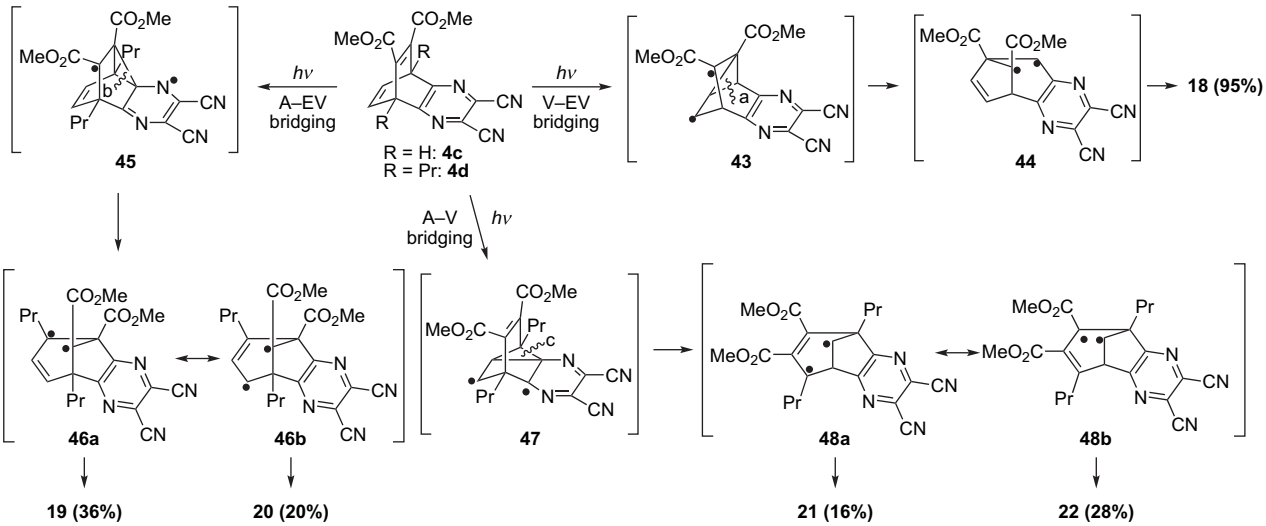
δ 4.63 was observed as singlet. Nevertheless, the inefficiency of **4c** to initiate A–EV bridging can be attributed to the synergistic effect of the electron-withdrawing ester group and the electronegativity of nitrogen, which weaken the bonds of the cyclopropyl ring;[5,22] thus, V–EV bridging is favored wherein the strength of the bond in the cyclopropyl moiety is only affected by the ester group. In the case of **4d**, which follows the ADPM route, the preferred bridging is facilitated by the presence of the propyl group, which stabilizes the radicaloid intermediates as depicted in Scheme 12 for its plausible mechanism. Pyrazinobarrelene **4c** generates the intermediates **43** and **44**. Closure of diradical **44** produces **18** in isolated yield of 95%. In the case of **4d**, the initial A–EV bridging can lead to diradical species **45** despite the fact that it involves disruption of aromaticity of pyrazine ring; however, the presence of the polar groups may have enhanced the regioselectivity through conjugative stabilization of diradical intermediates.[1b,6,8,22,23] This species can undergo cleavage of cyclopropyl ring at bond 'b' to relieve ring strain and regenerate aromaticity and form 1,3-diradical **46** (resonance structures **46a** and **46b**) to furnish SBs **19** (36%) and **20** (20%), respectively. A–V bridging of **4d** generates the diradical intermediate **47** and forms the secondary intermediate **48** (resonance structures **48a** and **48b**) upon breaking of cyclopropyl ring at bond 'c'; closure of diradical **48** affords SBs **21** (16%) and **22** (28%), respectively. The exclusive formation of DPM photoproduct **18** from **4c** via V–EV bridging and the higher overall ADPM yield from **4d** via A–EV bridging reflect the radical-stabilizing ability of the polar ester groups.[3b,4b,5,16d,22,24]

The product distributions of **19** (36%) and **20** (20%) are explicable in terms of the relatively higher stability of bis-tertiary-radical-centered resonance structure of **46a** over **46b**, which has tertiary and secondary radical centers. In a similar fashion, the relatively higher yield of **22** over **21** may be attributed to the noticeably higher stabilizing effect of ester moiety at the tertiary radical center of **48b** over that of propyl group at the tertiary radical center of **48a**. The greater stability of diradical **45** with ester group-substituted tertiary radical center in comparison with **47** bearing a secondary radical center justifies the preference for the initial pyrazino-diester vinyl bridging leading to **19** and **20** (56%) over pyrazino-vinyl mode, which leads to **21** and **22** (44%).

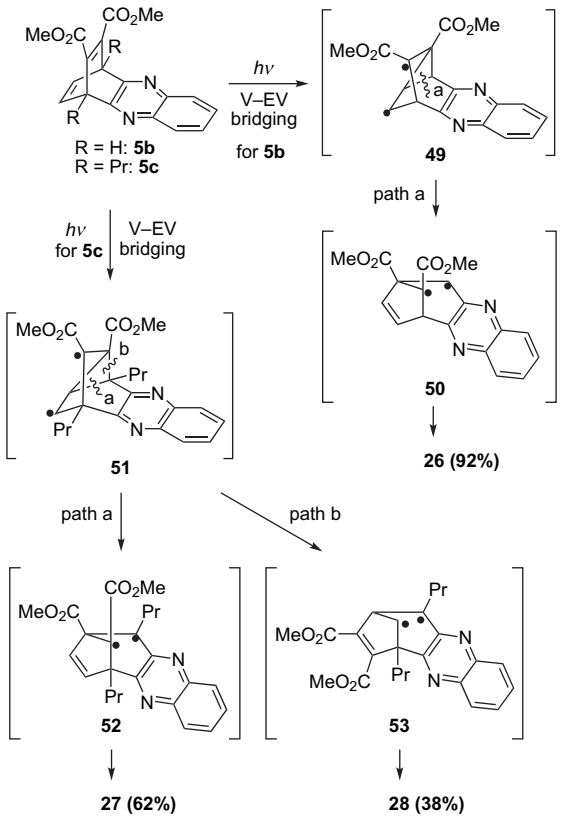
2.4.3. *Bridging modes and photorearrangements of quinoxalinobarrelenes **5a–c***

Quinoxalinobarrelene **5a** exhibits a bridging preference and product distribution similar to that of pyrazinobarrelene **4a**. Like SBs **13**–**15** in **4a**, SB **23** can be generated from an intermediate similar to **39** via V–V bridging whereas SBs **24** and **25** can be generated from intermediates similar to **41** and **42** via A–V bridging, respectively. Although we irradiated the molecule at the excitation region of quinoxaline (See Supplementary data), the regioselectivity was dominated via V–V bridging. Quinoxalines are known to participate in intramolecular energy transfer to homodiene moiety;[29] however, it remains to be answered how this energy is transferred to the homodiene moiety. Nevertheless, the bridging preference of barrelene **5a** is explicable in terms of energy minimization of the perturbed triplet state after the primary bonding interaction. If we assume that the ester moieties exhibit the same structural effect on the triplet energies of quinoxaline and homodiene moieties during bridging, then the initial V–V bonding will give rise to triplet energy of *cisoid* butadiene (T_1=53.5 kcal/mol) whereas initial bonding of quinoxaline with the vinyl group will give rise to a vinylquinoxaline structure with T_1 energy close to 59 kcal/mol,[10] 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, which generates SB under direct or sensitized condition via V–V bridging.[2b] It is pertinent to mention here that quinoxaline (T_1=60.6 kcal/mol)[25,26] and naphthalene (T_1=60.9 kcal/mol)[20b] have comparable triplet energies. Furthermore, the driving force for the transfer of triplet energy to the vinylic moiety from the quinoxalino group in **5a** is more likely since by approximation approach the heteroaromatic group turned out to have higher triplet energy than the *cisoid* butadiene moiety. In our previous report,[10] we also noticed that the DPM route of unsubstituted quinoxalinobarrelene **2** (vide supra) is much favored over ADPM. Constellations of ester groups[17a,24] at the vinylic moieties of **5b** and **5c** further enhanced the V–EV bridging preference of these barrelenes with **5b** furnishing SB **26** in 92% and **5c** affording SBs **27** and **28** in 62% and 38%, respectively. The chemoselective formation of **26** from **5b** via V–VE bridging can also be interpreted by the electron-withdrawing effect of ester and nitrogen, which disfavor A–V bonding.[5,22]

Plausible reaction mechanisms for **5b**,**c** photorearrangements are depicted in Scheme 13. Initial V–EV bridging of **5b** generates the diradicaloid intermediate **49**; cleavage of bond 'a' affords the secondary diradicaloid intermediate **50**, which ultimately closes to produce the photoproduct **26**. Comparing the two possible modes 'a' and 'b' for the cleavage of the cyclopropane ring of biradical species **51**, we can expect that path a leading to **27** (62%) will be



Scheme 12. Conceivable photorearrangement of barrelenes **4c**,**d**.



Scheme 13. Conceivable photorearrangements of **5b**,**c**.

more favored than path b leading to SB **28** (38%) as a result of higher stability of biradical species **52** over **53**. The experimental results confirm this fact.

*2.4.4. Bridging mode and photorearrangement of benzo[g]quinoxalinobarrelenes **6a–c***

Benzoquinoxalinobarrelene **6a**, which is not tethered with diester functionalities, was insensitive to photochemical reactions either under direct or sensitized conditions. The inertness of **6a** can be ascribed either to the minimal excitation energy, which is insufficient to overcome the energy barrier during the initial bridging mode or to rapid intersystem crossing of **6** (T_1 (π,π^*)$\rightarrow$ S_0) back to the ground state.[27] Also, the lower triplet energy of benzoquinoxalinobarrelene, which is expected to be similar to 2,3-anthrabarrelene (T_1=43 kcal/mol)[21] reduces the driving force for intramolecular energy transfer to the homodiene moiety (T_1=53.5 kcal/mol). In the cases of barrelenes **6b** and **6c**, which generate the photoproducts via V–EV bridging, the plausible mechanisms for the photoreactions can be envisaged to be similar to that of **5b**,**c** (vide supra); we observed similar product distributions. The success of the current reactions of **6b** and **6c** is presumably due to the presence of ester groups in the vinyl moiety, which facilitate the intramolecular triplet energy transfer to this site of the molecule from the benzoquinoxaline moiety.

*2.4.5. Bridging mode and photorearrangement of benzo[f,h]quinoxalinobarrelenes **7a**,**b***

Like the barrelene systems previously discussed, the bridging preferences of barrelenes **7a** and **7b** can also be explained in terms of stabilities of biradical species and the possibility for intramolecular energy transfer since the benzo[*f*,*h*]quinoxaline moiety of **7a** and **7b** have higher triplet energy than the homodiene moiety.[20b,25] In **7a**, the transfer of triplet energy to the homodiene moiety may not be very effective due to extensive delocalization of energy to the heteroaromatic site; as a result, aryl–vinyl bridging is preferred. But with the attachment of diester moiety on the vinyl group as in **7b**, which lowers the triplet energy of the homodiene moiety,[17a] vinyl–vinyl bonding becomes the dominant mode of bridging step. The plausible mechanisms for the photorearrangement of these barrelene systems are depicted in Scheme 14. SB **32** is formed by DPM rearrangement via intermediates **55**–**57** whereas **33** and **34** are formed by ADPM route via intermediates **54** and **58a**,**b**. In barrelene **7a**, the biradical **54** (E=H) leading to ADPM products **33** and **34** is more stabilized by the dibenzo[*f*,*h*]quinoxalino ring through a significant degree of delocalization of spin density from carbon to neighboring nitrogen atom, though the aromaticity of the heteroaromatic ring is partially broken. The marginal difference in the relative yields of **33** (major) and **34** (minor) can be attributed to the extra stabilization of **58a** compared to **58b** brought about by the presence of tertiary radical center. On the contrary, in the reaction of barrelene **7b**, the biradical **55** (E=CO_2Me) leading to DPM products **35** and **36**, is more stabilized by the ester group without disrupting the aromaticity of the heteroaromatic ring. Furthermore, the formation of **35** is noticeably higher than that of **36** due to the relatively higher stability of **56** over **57** (E=CO_2Me) as a result of the polar nature and radical-stabilizing ability of ester group at the radical center of **56**.[24]

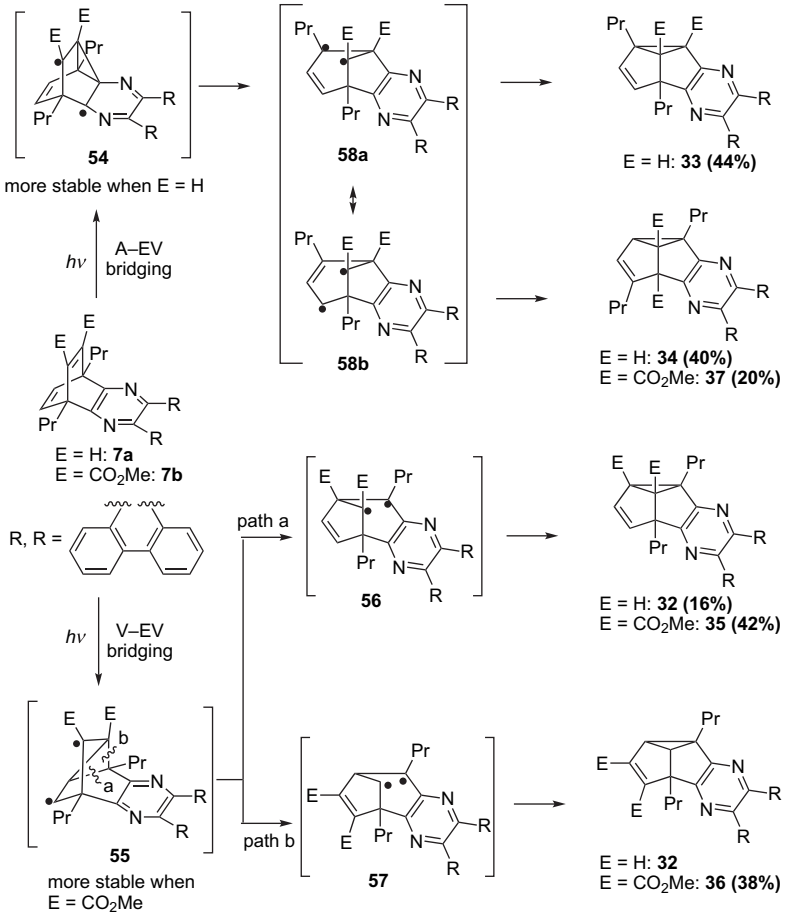
3. Conclusions

In summary, we have disclosed the photochemical behavior of heteroarene-fused barrelenes **4**–**7**. The presence of polar substituents such as the nitrile and the ester moieties strongly induced the chemoselectivity of photorearrangement. In addition, the nitrogen atoms in the aromatic moieties of these barrelene systems influenced the multiplicities of the excited state; the observed photoproducts were derived from the triplet excited state although at this stage we cannot account, which triplet state (n,π^* or π,π) is involved. Furthermore, we were able to account reasonably the bridging preferences of **4** and **5** in terms of minimum triplet energies based on Zimmerman's bridging hypothesis. Product distributions of barrelenes **4**–**7** were ascribed strongly through radical-stabilizing effects of polar and non-polar substituents as exemplified in the plausible mechanisms. It appears that steric factor exhibits a minor influence on the observed product distributions. The propyl group, for example, may have contributed to the selectivity of the process by stabilizing the incipient diradicaloid intermediates.

4. Experimental section

4.1. Dimethyl 7,8-dioxobicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (8b)

A powder solid of $NaBH_4$ (0.37 g, 9.73 mmol) was added slowly to a cooled (0 °C) solution of **38** (0.960 g, 3.24 mmol) in dry methanol (20 mL). The resulting mixture was stirred for 15 min and then quenched with NH_4Cl solution. After removing the solvent under reduced pressure, the residue was added with brine solution and the resulting mixture was extracted with ethyl acetate (3×). The organic layers were collected and the solvent was removed in a rotavap. The yellow oily residue was added with acetone (15 mL) and 4 N NH_4Cl (15 mL), and the mixture was stirred for 24 h. After solvent workup, the residue was mixed with *o*-iodoxybenzoic acid (IBX) in dichloromethane and heated under reflux for 8 h. The resulting solution was filtered, washed with ether, and further purified by column chromatography to yield a yellow oily product, **8b** (507 mg, 63%).



Scheme 14. Plausible mechanism for the photorearrangement of barrelenes **7a**,**b**.

*4.1.1. Dimethyl-7,8-dioxobicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**8b**)*

IR (neat): 3050, 2957, 1732, 1717, 1652, 1436, 1275, 1070, 744 cm^{-1}; UV (MeOH): λ_{max}=432 nm (3.2×10^2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.73 (dd, J=3.2, 4.4 Hz, 2H), 4.57 (dd, J=3.2, 4.4 Hz, 2H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 177.1, 163.6, 136.7, 130.6, 53.4, 53.1; MS (EI, 70 eV): m/z (%) 250 (0.3) [M^+], 231 (4), 221 (3), 195 (10), 163 (100), 104 (13), 78 (22); HRMS (EI) calcd for $C_{12}H_{10}O_6$: [M^+] 250.0477; found: 250.0450.

4.2. 5,8-Dipropyl-5,8-dihydro-5,8-ethenoquinoxaline (4a)

A solution of **8a** (513 mg, 2.35 mmol) in benzene (5 mL) was added with ethylenediamine **9** (226.2 mg, 3.71 mM in benzene) and the resulting mixture was stirred for 54 h. After removing the excess ethylenediamine by raising the temperature, the mixture was cooled to obtain a crude product (150 mg), which was filtered and washed with hexane. The resulting organic layer was concentrated under reduced pressure. Column chromatography of the residue on silica gel (hexanes/ethyl acetate, 15:1) afforded a solid (402 mg). All the products were combined (552 mg) and further recrystallized from hexane to obtain a crystalline solid **49** (mp 67–68 °C) in 97% yield.

To a solution of **49** (40 mg, 0.16 mmol) in toluene (4 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (120 mg, 0.53 mmol), and then the reaction mixture was stirred and heated at 120 °C under N_2 for 21 h. The resulting mixture was filtered to remove the oxidant, and the filtrate was concentrated in vacuo and separated in a silica gel column (hexanes/ethyl acetate, 15:1) to obtain a crystalline solid **4a** (mp 96–97 °C) in 17% yield.

*4.2.1. 5,8-Dipropyl-1,2,3,4,5,8-hexahydro-5,8-ethenoquinoxaline (**49**)*

IR (neat) 3040, 2950, 2860, 1640, 1470, 1390, 1345, 1270, 1250, 1140, 1110, 980, 910, 900, 830, 800, 730, 700 cm^{-1}; UV (MeOH) λ_{max}=331.2 nm (3.4×10^2), 232.2 (2.8×10^3); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.29 (s, 4H), 3.37 (s, 4H), 2.02–1.98 (m, 4H), 1.59–1.53 (m, 4H), 1.07 (t, J=7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 158.3, 136.8, 53.4, 44.8, 31.0, 18.0, 14.8; MS (EI, 75 eV): m/z (%) 242 (50) [M^+], 227 (30), 214 (48), 213 (42), 199 (32), 162 (33), 133 (100), 91 (25). Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.53; H, 9.29; N, 11.37.

*4.2.2. 5,8-Dipropyl-5,8-dihydro-5,8-ethenoquinoxaline (**4a**)*

IR (Nujol) 3040, 2960, 2920, 2870, 2240, 1740, 1640, 1580, 1545, 1430, 1330, 1250, 1210, 1140, 1110, 1100, 1040, 1020, 950, 910, 710 cm^{-1}; UV (MeOH) λ_{max}=280.4 nm (3.3×10^3); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.82 (s, 2H), 6.74 (s, 4H), 2.38–2.34 (m, 4H), 1.76–1.70 (m, 4H), 1.15 (t, J=7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.7, 142.7, 134.9, 55.8, 31.2, 18.3, 14.9; MS (EI, 75 eV) m/z (%) 240 (40) [M^+], 225 (8), 212 (14), 211 (100), 197 (15), 182 (10), 169 (24), 168 (9), 143 (7), 91 (6). Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.96; H, 8.39; N, 11.66. Found: C, 79.46; H, 8.55; N, 11.36.

*4.2.3. 5,8-Dipropyl-5,8-dihydro-5,8-ethenoquinoxaline-2,3-dicarbonitrile (**4b**)*

A solution of compound **8a** (191 mg, 0.876 mmol) in ethanol (5 mL) containing catalytic amount of *p*-TSA and diaminomaleonitrile (**10**) (184 mg, 1.7 mmol) was heated at 60 °C under nitrogen for 20 h. After solvent workup, the resulting product was subjected to column chromatography (hexanes/ethyl

acetate 30:1) to obtain a white solid, which yielded upon crystallization in cyclohexane/dichloromethane a crystalline solid **4b** (mp 138–140 °C) in 64% yield. IR (Nujol) 3040, 2960, 2920, 2870, 2240, 1740, 1640, 1580, 1545, 1430, 1330, 1250, 1210, 1140, 1110, 1100, 1040, 1020, 950, 910, 710 cm^{-1}; UV (MeOH) λ_{max}=298.0 nm (1.6×10^4), 207.8 (3.2×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.77 (s, 4H), 2.36–2.32 (m, 4H), 1.73–1.67 (m, 4H), 1.16 (t, J=7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.9, 142.1, 125.8, 113.9, 56.2, 30.6, 18.1, 14.6; MS (EI, 75 eV) m/z (%) 290 (55) [M^+] 275 (9), 262 (20), 261 (100), 248 (20), 247 (30), 233 (12), 220 (14), 219 (82), 207 (8), 206 (9), 205 (7), 193 (14). Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.29. Found: C, 75.03; H, 6.33; N, 19.35.

4.2.4. Dimethyl 2,3-dicyano-5,8-dihydro-5,8-ethenoquinoxaline-6,7-dicarboxylate (*4c*)

Compound **8b** (56 mg, 0.21 mmol, 1 equiv) in MeOH (15 mL) was mixed with diamine **10** (35 mg, 0.32 mmol, 1.5 equiv) 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 1:2) and yielded upon crystallization from dichloromethane a white crystalline solid **4c**(54 mg) in 80% yield. IR (neat) 3003, 2844, 1731, 1652, 1435, 1290, 1123, 1075, 746 cm^{-1}; UV (MeOH) λ_{max}=290 nm (4×10^3), 243 (4.8×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.14 (dd, J=3.2, 4.4 Hz, 2H), 5.43 (dd, J=3.2, 4.4 Hz, 2H), 3.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.7, 161.1, 144.9, 137.9, 127.7, 113.1, 53.1, 50.5; MS (EI, 75 eV) m/z (%) 323 (12) [M^++H], 322 (58), 264 (45), 262 (43), 235 (23), 219 (100), 205 (17), 128 (30); HRMS (EI) calcd for $C_{16}H_{10}N_4O_4$: [M^+] 322.0702, found: 322.0692.

4.2.5. Dimethyl 2,3-dicyano-5,8-dipropyl-5,8-dihydro-5,8-ethenoquinoxaline-6,7-dicarboxylate (*4d*)

A solution of **8c** (1.882 g, 5.57 mmol) in ethanol (30 mL) was added with diamine **10** (0.73 g, 6.67 mmol) and refluxed under nitrogen for 15 h. The reaction mixture was concentrated in vacuo and chromatographed using $CHCl_3$ as eluant to obtain a solid (2.052 g), which upon recrystallization from dichloromethane/cyclohexane yielded barrelene **4d** (mp 117–118 °C) in 85% yield. IR (CCl_4) 2970, 2950, 2930, 2875, 1735, 1585, 1550, 1465, 1435, 1330, 1290, 1255, 1215, 1155, 1135, 1095, 1045, 1005, 975 cm^{-1}; UV (MeOH) λ_{max}=294.5 nm (1.7×10^4), 204.8 (3.6×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.94 (s, 2H), 3.76 (s, 6H), 2.50–2.44 (m, 4H), 1.70–1.51 (m, 4H), 1.15 (t, J=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 164.4, 163.9, 148.9, 141.5, 126.7, 113.4, 56.7, 52.6, 28.6, 18.2, 14.8; MS (EI, 75 eV) m/z (%) 406 (24) [M^+], 375 (24), 374 (48), 347 (38), 346 (100), 332 (12), 331 (13), 315 (20), 314 (25), 302 (12), 288 (20), 287 (95), 273 (21), 257 (18), 245 (19), 231 (12), 218 (9), 193 (16), 111 (16), 59 (30), 43 (14), 41 (17), 39 (15). Anal. Calcd for $C_{22}H_{22}N_4O_4$: C, 65.01; H, 5.46; N, 13.78. Found: C, 64.89; H, 5.50; N, 13.69.

4.2.6. 1,4-Dipropyl-1,4-dihydro-1,4-ethenophenazine (*5a*)

Compound **8a** (251 mg, 1.15 mmol) dissolved in ethanol (8 mL) was added with phenylene diamine **11** (159 mg, 1.38 mmol) and catalytic amount of *p*-TSA, and then heated under nitrogen at 70 °C for 12 h. The reaction mixture was cooled, filtered, and washed with ethanol to obtain **5a** (332 mg), which was further recrystallized from cyclohexane yielding the barrelene **5a** (mp 133–135 °C) in 99% yield. IR (Nujol) 2950, 2920, 2850, 1460, 1375, 1215, 760, 670 cm^{-1}; UV (MeOH) λ_{max}=325 nm (7.0×10^3), 314.8 (8.6×10^3), 249.7 (1.5×10^4), 210.9 (3.6×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.90–7.87 (m, 2H), 7.59–7.55 (m, 2H), 6.72 (s, 4H), 2.47–2.43 (m, 4H), 1.87–1.71 (m, 4H), 1.20 (t, J=7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 160.9, 141.7, 137.2, 128.3, 128.2, 55.1, 31.4, 18.4, 15.1; MS (EI, 75 eV) m/z (%) 290 (42) [M^+], 275 (7), 262 (28), 261 (100), 248 (11), 247 (36), 232 (10), 231 (12), 219 (30), 218 (18), 205 (10), 193 (6), 116 (9). Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.91; H, 7.66; N, 9.40.

4.2.7. Dimethyl 1,4-dihydro-1,4-ethenophenazine-2,3-dicarboxylate (*5b*)

A solution of **8b** (35 mg, 0.13 mmol, 1 equiv) in methanol (8 mL) was mixed with diaminobenzene **11** (18 mg, 0.16 mmol, 1.2 equiv) and heated at 50 °C until the reaction was complete. After removing the solvent in vacuo, the crude product was purified by column chromatography (ethyl acetate/hexanes 1:4) to obtain a white powder, which was further recrystallized from dichloromethane yielding **5b** (40 mg) in 95% yield. IR (neat) 2952, 1718, 1645, 1435, 1268, 1208, 763 cm^{-1}; UV (MeOH) λ_{max}=331 nm (4.6×10^3), 317 (5.2×10^3), 247 (1.27×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.89–7.91 (m, 2H), 7.64–7.66 (m, 2H), 7.08 (dd, J=3.2, 4.4 Hz, 2H), 5.34 (dd, J=3.2, 4.4 Hz, 2H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 164.8, 155.6, 145.2, 138.2, 137.6, 129.4, 128.5, 52.7, 50.8; MS (EI, 75 eV) 323 (18) [M^++H], 322 (67), 263 (82), 235 (70), 231 (38), 219 (100), 206 (57), 204 (47); HRMS (EI) calcd for $C_{18}H_{14}N_2O_4$ (M^+): 322.0954, found: 322.0961.

4.2.8. Dimethyl 1,4-dipropyl-1,4-dihydro-1,4-ethenophenazine-2,3-dicarboxylate (*5c*)

A solution of **8c** (2.906 g, 8.71 mmol) in methanol (30 mL) was added with diamine **11** (1.127 g, 10.44 mmol) and catalytic amount of *p*-TSA, and then refluxed under nitrogen for 3 h. The mixture was cooled, filtered, and then worked up to obtain **5c** (3.035 g, 94%). A white crystalline solid (mp 162–164 °C) of **5c** was obtained upon recrystallization from dichloromethane/hexane. IR (CCl_4) 3075, 2970, 2920, 2880, 1735, 1630, 1590, 1470, 1460, 1440, 1310, 1260, 1140, 1100, 1070, 960, 780, 740, 610 cm^{-1}; UV (CH_3OH) λ_{max}=314 nm (1.1×10^4), 247.3 (3.2×10^4), 208.2 (4.7×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.96–7.83 (m, 4H), 6.85 (s, 2H), 3.72 (s, 6H), 2.56 (t, J=8 Hz, 4H), 1.94–1.38 (m, 4H), 1.15 (t, J=6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.2, 158.2, 148.7, 140.9, 137.1, 128.6, 128.4, 55.8, 52.2, 29.4, 15.1; MS (EI, 75 eV) m/z (%) 406 (100) [M^+], 377 (20), 347 (51), 346 (53), 331 (10), 317 (39), 303 (20), 287 (49), 245 (18). Anal. Calcd for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.07; H, 6.43; N, 7.02.

4.2.9. 1,4-Dipropyl-1,4-dihydro-1,4-ethenobenzo[b]phenazine (*6a*)

Following a similar procedure described in **5a**, compound **8a** (96 mg, 0.44 mmol) in ethanol (5 mL) and diamine **12** (73 mg, 0.46 mmol) afforded a white, cloudy solution after refluxing for 8 h. Workup of the resulting mixture afforded **6a** (127 mg, 85%), which can be recrystallized from dichloromethane/hexane as a white crystalline solid (mp 118–120 °C). IR (KBr) 3060, 3030, 2950, 2920, 2860, 1600, 1560, 1460, 1445, 1430, 1350, 1300, 1170, 1150, 1110, 960, 910, 820, 750, 720, 690, 680 cm^{-1}; UV (CH_3OH) λ_{max}=363.4 (2.2×10^4), 346.5 (1.9×10^4), 275.6 (1.2×10^4), 258.6 (9.0×10^4), 233.8 (9.6×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.40 (s, 2H), 8.01–7.99 (m, 2H), 7.49–7.47 (m, 2H), 6.69 (s, 4H), 2.48–2.44 (m, 4H), 1.79–1.69 (m, 4H), 1.21 (t, J=7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 160.2, 140.9, 135.1, 133.1, 128.1, 126.2, 125.8, 54.8, 31.4, 18.4, 15.1; MS (EI, 75 eV) m/z (%) 340 (72) [M^+], 325 (12), 312 (36), 311 (100), 297 (48), 282 (14), 281 (14), 269 (23), 268 (18). Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.70; H, 7.16; N, 8.06.

4.2.10. Dimethyl 1,4-dihydro-1,4-ethenobenzo[b]phenazine-2,3-dicarboxylate (*6b*)

Compound **8b** (80 mg, 0.30 mmol, 1 equiv) in methanol (8 mL) was added with diamine **12** (47 mg, 0.30 mmol, 1 equiv) and heated under reflux until the reaction was complete. After solvent workup and purification by recrystallization in dichloromethane, compound **6b** (53 mg) was obtained in 48% yield. IR (neat): 3054, 2955, 1713, 1644, 1434, 1316, 1274, 1167, 1123, 880, 745 cm^{-1}; UV (MeOH)

λ_{max}=366 nm (5×103), 350 (4.2×103), 275 (1.47×104); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.43 (s, 2H), 8.04–8.06 (m, 2H), 7.52–7.56 (m, 2H), 7.09 (dd, *J*=2.8, 3.6 Hz, 2H), 5.34 (dd, *J*=2.8, 3.6 Hz, 2H), 3.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 164.8, 154.7, 144.4, 136.7, 135.5, 133.5, 128.2, 126.8, 126.5, 52.7, 50.6; MS (EI, 75 eV) *m*/*z* (%) 373 (26) [M^++H], 372 (100), 313 (51), 312 (31), 255 (32), 254 (42), 253 (20), 230 (30), 178 (17); HRMS (EI) calcd for $C_{22}H_{16}N_2O_4$ (M^+): 372.1110, found: 372.1111.

4.2.11. Dimethyl 1,4-dipropyl-1,4-dihydro-1,4-ethenobenzo-[b]phenazine-2,3-dicarboxylate (**6c**)

Following the procedure described in **5c**, compound **8c** (811 mg, 2.43 mmol) in ethanol (25 mL) was reacted with diamine **12** (422 mg, 2.67 mmol), and after workup and recrystallization from dichloromethane/hexane furnished **6c** (1.083 g, 98%) (mp 203–204 °C). IR (CCl_4) 3050, 2960, 2930, 2870, 1730, 1550, 1430, 1310, 1255, 1100, 1005, 980, 885, 810–740 cm^{-1}; UV (CH_3OH) λ_{max}=364.6 nm (5.9×10^2), 276.8 (4.5×10^3), 226.2 (2.6×10^3); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.42 (s, 2H), 8.04–7.90 (m, 2H), 7.56–7.38 (m, 2H), 6.82 (s, 2H), 3.72 (s, 6H), 2.58 (t, *J*=8 Hz, 4H), 1.96–1.44 (m, 4H), 1.16 (t, *J*=7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.3, 157.4, 147.l9, 140.3, 134.8, 133.3, 128, 126.6, 125.9, 55.6, 52.3, 29.5, 18.5, 15.2; MS (EI, 75 eV) *m*/*z* (%) 456 (100) [M^+], 441 (8), 427 (44), 413 (42), 397 (55), 398 (32), 381 (16), 367 (33), 365 (22), 337 (43), 309 (20), 295 (14), 281 (12), 268 (11); HRMS (EI) calcd for $C_{28}H_{28}N_2O_4$ (M^+): 456.2049, found: 456.2038.

4.2.12. 10,13-Dipropyl-10,13-dihydro-10,13-ethenobenzo[f]-tetraphene (**7a**)

A solution of **8a** (250 mg, 1.15 mmol) in benzene (30 mL) was added with phenanthrene-9,10-diamine (270 mg, 1.3 mmol) and catalytic amount of *p*-TSA, and then refluxed under nitrogen for 12 h. To complete the reaction, another 50 mg of diamine was added to the reaction mixture and refluxing was continued for another 12 h. After solvent workup, a yellow liquid (312 mg, 70%) was obtained, which can be recrystallized from dichloromethane/hexanes as a yellow crystalline solid of **7a** (mp 223–225 °C). IR (KBr) 3050, 2960, 2930, 2870, 1610, 1585, 1495, 1465, 1450, 1410, 1385, 1330, 1275, 1165, 1145, 1130, 1120, 1100, 1040, 975, 955, 940, 885, 860, 760, 730 cm^{-1}; UV (CH_3OH) λ_{max}=351 nm (4.6×10^4), 335 (3.4×20^4), 257 (1.4×10^5), 223 (1.1×105); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.23–9.2 (m, 2H), 8.63–8.61 (m, 2H), 7.72–7.69 (m, 4H), 6.81 (s, 4H), 2.63–2.59 (m, 4H), 1.92–2.59 (m, 4H), 1.28 (t, *J*=7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 161.5, 142.8, 133.0, 131.0, 130.8, 128.0, 127.5, 124.6, 122.5, 56.0, 30.1, 18.6, 15.3; MS (EI, 75 eV) *m*/*z* (%) 390 (61) [M^+], 375 (4), 362 (25), 361 (100), 347 (18), 331 (14), 319 (20), 305 (6), 293 (6); HRMS (EI) calcd for $C_{28}H_{26}N_2$ (M^+): 390.2096, found: 390.2089.

4.2.13. Dimethyl 10,13-dipropyl-10,13-dihydro-10,13-ethenobenzo[f]tetraphene-11,12-dicarboxylate (**7b**)

A solution of **8c** (503 mg, 1.51 mmol) in acetonitrile (25 mL) was added with phenanthrene-9,10-diamine (346 mg, 1.66 mmol) and catalytic amount of *p*-TSA, and then refluxed for 17 h. After solvent workup, the product was recrystallized from dichloromethane to obtain a white crystalline solid of **7b** (737 mg, 97%) (mp 259–261 °C). IR (KBr) 3070, 3020, 2970, 2930, 2870, 1730, 1625, 1585, 1500, 1460, 1435, 1420, 1385, 1330, 1260, 1200, 1170, 1140, 1100, 1065, 1050, 860, 850, 800, 770, 730, 630 cm^{-1}; UV (CH_3OH) λ_{max}=358 nm (2.1×10^3), 315 (1.7×10^3), 342 (1.6×10^3), 255.4 (6.4×10^3); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.2–9.18 (m, 2H), 8.62–8.60 (m, 2H), 7.73–7.70 (m, 4H), 6.98 (s, 2H), 3.75 (s, 6H), 2.79–2.67 (m, 4H), 2.05–1.90 (m, 2H), 1.78–1.63 (m, 2H), 1.26 (t, *J*=8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.8, 158.7, 150.1, 142.0, 133.7, 131.0, 130.2, 128.3, 127.2, 125.1, 122.6, 56.6, 52.3, 29.5, 18.7, 15.3; MS (EI, 75 eV) *m*/*z* (%) 506 (100) [M^+], 477 (44), 463 (10), 447 (35), 446 (31), 431 (7), 417 (26), 403 (9), 387 (34), 373 (9), 359 (11), 358 (11), 345 (11), 331 (10), 319 (9); HRMS (EI) calcd for $C_{32}H_{30}N_2O_4$ (M^+): 506.2206, found: 506.2215.

4.3. General procedures for photorearrangement

Unless stated otherwise, photoreactants were placed in Pyrex tubes and dissolved either in deuterated benzene (for direct irradiation) or in deuterated acetone (for sensitized irradiation). The resulting mixtures were degassed either by sonication or by bubbling argon gas (1 h) and then irradiated with 350 nm light until the reaction was complete. Solvents were removed under reduced pressure and purification of crude products was done by column chromatography using ethyl acetate/hexanes as eluant. Unless otherwise specified, relative yields of photoproducts were determined by ^{1}H NMR integrations of the mixture.

4.3.1. Irradiation of **4a**

Irradiation of **4a** (10 mg) in C_6D_6 (2 mL) with 350 nm light for 4 h afforded photoproducts **13**–**15** with relative yields of 53:25:22 based on ^{1}H NMR integrations and 2D NMR. The crude mixture was separated in a column (hexanes/ethyl acetate 15:1) to obtain **4a** (1 mg), **14** (1.5 mg, 15%), and mixture of **13** and **15** (3.5 mg). The mixture was further separated in a column using the same eluant to obtain **13** (1.8 mg) and non-separable mixture of **13** and **15** (0.4 mg).

4.3.1.1. 2b,6b-Dipropyl-2a,2b,6b,6c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]pyrazine (**13**).

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 7.93 and 7.84 (AB, *J*=2.8 Hz, 2H), 5.41 (d, *J*=5 Hz, 1H), 5.09 (d, *J*=5, 3 Hz, 1H), 2.68 (d, *J*=6.4 Hz, 1H), 2.46 (t, *J*=6.4, 3 Hz, 1H), 2.36–1.91 (m, 4H), 1.82–1.46 (m, 2H), 1.40–1.27 (m, 2H), 0.92 (t, *J*=6.4 Hz, 6H).

4.3.1.2. 2a,6b-Dipropyl-2a,2b,6b,6c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]pyrazine (**14**).

IR (neat) 3050, 2970, 2940, 2880, 1460, 1400, 1370, 760 cm^{-1}; UV (CH_3OH) λ_{max}=285.0 nm (3.3×10^3), 230.1 (3.4×10^3); ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 8.06 and 7.97 (AB, *J*=2.9 Hz, 2H), 5.44 (d, *J*=5 Hz, 1H), 5.08 (d, *J*=5 Hz, 1H), 2.95 (d, *J*=6.3 Hz, 1H), 2.64 (d, *J*=6.4 Hz, 1H), 2.24–2.19 (m, 1H), 2.06–2.00 (m, 1H), 1.62–1.41 (m, 6H), 1.01 (t, *J*=7.3 Hz, 3H), 0.92 (t, *J*=7.3 Hz, 3H); MS (EI, 75 eV) *m*/*z* (%) 240 (69) [M^+], 225 (10), 212 (21), 211 (100), 198 (39), 197 (63), 183 (10), 182 (20), 181 (11), 170 (19), 169 (69), 168 (23), 155 (13), 143 (16), 128 (6).

4.3.1.3. 1,2b-Dipropyl-2a,2b,6b,6c-tetrahydrocyclopropa[3,4]pentaleno[1,2-b]pyrazine (**15**).

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 8.10 and 8.00 (AB, *J*=3.2 Hz, 2H), 4.90 (d, *J*=5 Hz, 1H), 3.66 (d, *J*=6 Hz, 1H), 2.81 (t, *J*=6 Hz, 1H), 2.36 (dd, *J*=6, 5 Hz, 1H), 2.00–1.20 (m, 8H), 1.13 (t, *J*=6.4 Hz, 3H), 0.96 (t, *J*=6 Hz, 3H).

4.3.2. Irradiation of **4b**

A solution of **4b** (48 mg) in C_6D_6 (10 mL) was irradiated with 350 nm light for 4 h. From ^{1}H NMR integrations, photoproducts **16** and **17** were observed with a relative yield of 43:57. The photoproducts were separated by preparative TLC using benzene as eluant. Each distinct spot from TLC was scraped and dissolved in dichloromethane (20 mL). After filtration and solvent workup, photoproducts **16** (16 mg, 33%) and **17** (29 mg, 60%) were obtained. A similar result was observed when **4b** was irradiated under sensitized condition using deuterated acetone as solvent.

4.3.2.1. 2a,6b-Dipropyl-2a,2b,6b,6c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]pyrazine-4,5-dicarbonitrile (**16**).

IR (neat) 3060, 2980, 2940, 2880, 2250, 1590, 1550, 1470, 1410, 1385, 1340, 1280, 1200, 1170, 1115, 1100, 1020, 950, 900, 840, 800, 770, 720 cm^{-1}; UV

(CH_3OH) λ_{max}=278.5 nm (4.3×10^3), 205.9 (5.3×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.44 and 5.02 (AB, J=5 Hz, 2H), 3.28 and 3.15 (AB, J=5.8 Hz, 2H), 2.13–2.07 (m, 1H), 1.98–1.87 (m, 2H), 1.79–1.72 (m, 1H), 1.64–1.57 (m, 2H), 1.43–1.30 (m, 2H), 1.03–0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 165.2, 157.7, 134.8, 130.9, 129.4, 128.6, 113.9, 113.7, 64.8, 58.2, 57.3, 40.9, 35.8, 32.2, 21.3, 18.6, 14.4, 14.02; MS (EI, 75 eV) m/z (%) 290 (53) [M^+], 279 (23), 275 (13), 262 (28), 261 (92), 248 (26), 247 (82), 233 (12), 220 (19), 219 (100), 205 (11), 193 (8), 149 (11), 85 (13), 55 (25), 43 (36), 41 (33).

*4.3.2.2. 1,2b-Dipropyl-2a,2b,6b,6c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]pyrazine-4,5-dicarbonitrile (**17**).* IR (neat) 3020, 2970, 2940, 2880, 2240, 1620, 1550, 1470, 1380, 1330, 800, 780 cm^{-1}; UV (CH_3OH) λ_{max}=289.1 nm (1.1×10^4), 207 (1.6×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.27 (d, J=2.4 Hz, 1H), 3.93 (d, J=6.1 Hz, 1H), 3.49 (t, J=6.4 Hz, 1H), 2.91 (dd, J=2.4, 6.4 Hz, 1H), 2.19–1.31 (m, 8H), 0.95 (t, J=7.3 Hz, 3H), 0.90 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 162.4, 159.5, 148.5, 131.5, 128.9, 121.6, 113.9, 113.9, 54.9, 54.7, 47.9, 47.8, 33.1, 29.3, 20.5, 20.3, 14.2, 13.7; MS (EI, 75 eV) m/z (%) 290 (47) [M^+], 275 (13), 262 (24), 261 (100), 247 (20), 24.7 (17), 233 (12), 217 (80), 206 (8), 43 (10), 41 (13).

*4.3.3. Irradiation of **4c***

Following the general procedure, compound **4c** with 0.02 M concentration in benzene was degassed and irradiated to obtain semibullvalene **18** in 95% isolated yield.

*4.3.3.1. Dimethyl 4,5-dicyano-2b,6b-dihydrocyclopropa[3,4]pentaleno-[1,2-b]pyrazine-2a,6c-dicarboxylate (**18**).* IR (neat) 3009, 2956, 2852, 2230, 1734, 1652, 1439, 1338, 1246, 1139, 730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.74 (s, 3H), 3.85 (s, 3H), 4.63 (s, 1H), 4.73 (d, J=2.8 Hz, 1H), 5.72 (d, J=5.2 Hz, 1H), 5.87 (dd, J=2.8, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 45.4, 53.1, 53.4, 55.6, 59.4, 65.3, 113.0, 113.1, 125.4, 130.9, 131.8, 134.0, 153.9, 162.8, 165.9, 166.1; MS (EI, 75 eV) m/z (%) 323 (12) [M^++H], 322 (38), 294 (27), 291 (24), 280 (21), 265 (37), 264 (100), 260 (40); HRMS (EI) calcd for $C_{16}H_{10}N_4O_4$ (M^+): 322.0702, found: 322.0710.

*4.3.4. Irradiation of **4d***

A solution of **4d** (173 mg) in benzene (50 mL) was irradiated with 350 nm light for 10 h. Based on ^1H NMR integrations, four photoproducts **19**–**22** were observed with a relative yield of 20:36:21:28. After removal of solvent in a rotavap, the crude products were separated in a column (chloroform/ethyl acetate 30:1). Partial separation was obtained with the first fraction (41 mg) containing **20** and trace amount of **19** and **22** as checked by ^1H NMR. The second fraction (85 mg) contained a mixture of **21** and **22**, and trace amount of **20**. The third fraction (39 mg) contained non-characterizable photoproducts and the fourth fraction (3 mg) contained a mixture of **21** and **22**. All these fractions were further separated in a column (3×) to finally obtained **19** (1 mg), **20** (15 mg), **21** (4 mg), and **22** (9 mg). All the photoproducts were yellowish liquid, which cannot be recrystallized from cyclohexane/methanol solvents. Similar results were obtained when benzene was replaced with acetone during sensitized reaction.

*4.3.4.1. Dimethyl 4,5-dicyano-1,2b-dipropyl-2a,2b-dihydrocyclopropa-[3,4]pentaleno[1,2-b]pyrazine-6b,6c-dicarboxylate (**19**).* IR (CCl_4) 3030, 3000, 2960, 2935, 2875, 1735, 1615, 1550, 1465, 1455, 1435, 1415, 1330, 1255, 1225, 1200, 1160, 1140, 1095, 1005, 980, 910, 810–740, 630 cm^{-1}; UV (CH_3OH) λ_{max}=287.1 nm (1.0×10^3), 306.0 (1.6×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.31 (d, J=1.94 Hz, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 3.57 (d, J=1.64 Hz, 1H), 2.60–2.50 (m, 1H), 2.38–2.28 (m, 1H), 2.04–1.88 (m, 2H), 1.59–1.14 (m, 4H), 0.95 (t, J=7.3 Hz, 3H), 0.81 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 167.0, 166.3, 157.7, 155.4, 149.3, 132.2, 130.8, 121.1, 113.4, 69.4, 67.9, 55.6, 52.8, 52.7, 51.5, 30.3, 27.7, 20.6, 20.6, 20.2, 14.1, 13.6; MS (EI, 75 eV) m/z (%) 406 (22) [M^+], 375 (6), 246 (67), 331 (4), 314 (13), 287 (100), 273 (19), 259 (12), 257 (10), 245 (22), 231 (12), 86 (8), 84 (14), 59 (43), 49 (17), 29 (12).

*4.3.4.2. Dimethyl 4,5-dicyano-2a,6b-dipropyl-2a,6b-dihydrocyclopropa[3,4]pentaleno[1,2-b]pyrazine-2b,6c-dicarboxylate (**20**).* IR (CCl_4) 2960, 2930, 2875, 1740, 1640, 1550, 1465, 1455, 1435, 1380, 1330, 1250, 1225, 1215, 1160, 1090, 1065, 1005, 980, 630 cm^{-1}; UV (CH_3OH) λ_{max}=278.5 nm (4.3×10^3), 205.9 (5.3×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 5.71 and 5.57 (AB, J=5 Hz, 2H), 3.85 (s, 3H), 3.79 (s, 3H), 2.46–2.04 (m, 4H), 2.10–1.92 (m, 1H), 1.42–1.30 (1H), 1.30–1.07 (m, 2H), 1.00 (t, J=6.7 Hz, 3H), 0.93 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 166.9, 164.9, 163.7, 155.7, 137.6, 131.7, 130.9, 125.1, 113.5, 113.3, 68.9, 67.9, 59.9, 55.7, 53.0, 52.4, 30.4, 27.5, 21.1, 18.2, 14.5, 14.5; MS (EI, 75 eV) m/z (%) 406 (70) [M^+], 374 (47), 363 (42), 347 (65), 346 (100), 342 (18), 331 (26), 315 (77), 304 (33), 287 (74), 245 (66), 231 (21), 218 (19), 149 (21), 83 (33), 159 (75), 43 (38), 41 (59), 27 (37), 15 (45).

*4.3.4.3. Dimethyl 4,5-dicyano-2a,6b-dipropyl-2a,2b,6b,6c-tetrahydrocyclopropa[3,4]pentaleno[1,2-b]pyrazine-1,2-dicarboxylate (**21**).* IR (CCl_4) 3030, 3000, 2960, 2935, 2875, 2240, 1735, 1725, 1615, 1545, 1465, 1435, 1410, 1370, 1340, 1255, 1220, 1200, 1160, 1135, 1070, 1015, 980, 910 cm^{-1}; UV (CH_3OH) λ_{max}=263.3 nm (8.4×10^3), 204.9 (1.2×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.73 (s, 3H), 3.72 (s, 3H), 3.42 and 3.30 (AB, J=5.8 Hz, 2H), 2.48–2.32 (m, 2H), 2.03–1.90 (m, 2H), 1.6–1.4 (m, 4H), 0.06–0.94 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.6, 163.5, 162.2, 157.2, 140.2, 137.3, 132.3, 129.9, 113.5, 113.4, 64.7, 56.8, 55.4, 52.5, 52.4, 41.6, 34.4, 31.04, 20.8, 18.5, 14.3, 14.1; MS (EI, 75 eV) m/z (%) 406 (5) [M^+], 375 (26), 374 (100), 347 (6), 346 (6), 331 (10), 315 (12), 304 (12), 303 (11), 287 (9), 271 (9), 245 (12), 243 (10), 231 (6), 84 (14), 59 (23), 43 (14), 41 (18).

*4.3.4.4. Dimethyl 4,5-dicyano-1,2b-dipropyl-6b,6c-dihydrocyclopropa[3,4]pentaleno[1,2-b]pyrazine-2,2a(2bH)dicarboxylate (**22**).* IR (CCl_4) 3030, 3000, 2960, 2935, 2875, 2240, 1735, 1725, 1620, 1545, 1465, 1435, 1415, 1330, 1270, 1220, 1200, 1160, 1135, 1070, 1015, 980, 910 cm^{-1}; UV (CH_3OH) λ_{max}=275.2 nm (3.1×10^3), 204.2 (4.5×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.77 (s, 3H), 3.71 (s, 3H), 3.49 and 3.35 (AB, J=6.2 Hz, 2H), 2.28–2.13 (m, 2H), 2.08–1.88 (m, 2H), 1.74–1.23 (m, 2H), 0.99 (t, J=7.4 Hz, 3H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.1, 162.7, 162.5, 158.2, 144.3, 132.9, 132.4, 130.0, 113.5, 113.4, 65.5, 57.7, 52.6, 52.5, 47.3, 46.7, 32.9, 30.8, 20.3, 18.3, 14.7, 13.9; MS (EI, 75 eV) m/z (%) 406 (15) [M^+], 274 (15), 364 (5), 346 (17), 345 (21), 332 (11), 315 (13), 305 (10), 287 (11), 245 (10), 86 (60), 84 (100), 59 (16), 47 (24).

*4.3.5. Irradiation of **5a***

Compound **5a** (65 mg) in acetone (10 mL) was degassed under liquid nitrogen and then irradiated with 350 nm. The reaction was monitored by ^1H NMR and TLC every 30 min for 4 h. From ^1H NMR integrations semibullvalenes **23**–**25** were obtained with the relative yields of 71:13:16. After removing the solvent in a rotavap, the crude products were separated by eluting the sample with hexane followed by chloroform/hexane (1:1) to obtain two fractions A1 (a mixture of **23** and **24**) and A2 (a mixture of **24** and **25**). The resulting fractions were further separated in a column (hexane/ethyl acetate 5:1) to obtain **23** (18 mg) and **24** (9 mg). Compound **25** could not be isolated from the column. Similar results were obtained when acetone was replaced with benzene solvent during direct irradiation.

*4.3.5.1. 2b,8b-Dipropyl-2a,2b,8b,8c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]quinoxaline (**23**).* IR (CCl_4) 3060, 3030, 2960, 2930, 2870, 1680, 1660, 1580, 1465, 1470, 1415, 1375, 1340, 1115, 1100,

1025, 840, 835, 820–740 cm^{-1}; UV (CH_3OH) λ_{max}=278.5 nm (4.3×10^3), 205.9 (5.3×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.60–7.98 (m, 2H), 7.65–7.60 (m, 2H), 5.40 (s, 2H), 3.12 (d, J=8 Hz, 1H), 2.80 (d, J=6 Hz, 1H), 2.55–2.46 (m, 1H), 2.30–2.21 (m, 1H), 2.12–2.06 (m, 1H), 1.78–1.70 (m, 1H), 1.69–1.55 (m, 2H), 1.55–1.44 (m, 2H), 1.95 (t, J=8 Hz, 3H), 1.05 (t, J=8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 164.2, 156.8, 142,0, 140.6, 137.4, 128.7, 128.5, 128.0, 127.9, 125.5, 62.9, 59.9, 46.6, 44.4, 33.9, 32.8, 20.4, 18.9, 14.6, 14.4; MS (EI, 75 eV) m/z (%) 290 (71) [M^+], 275 (6), 262 (13), 261 (55), 248 (44), 247 (100), 232 (18), 231 (19), 219 (38), 220 (22), 205 (17), 182 (5), 106 (8), 86 (21), 84 (32).

*4.3.5.2. 2a,8b-Dipropyl-2a,2b,8b,8c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]quinoxaline (**24**).* IR (Nujol) 3060, 2960, 2930, 2860, 1500, 1465, 1380, 765 cm^{-1}; UV (CH_3OH) λ_{max}=323.3 nm (4.5×10^3), 249.6 (1.1×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.01–7.95 (m, 2H), 7.70–7.6 (m, 2H), 5.36 and 5.31 (AB, J=5 Hz, 2H), 3.08 and 3.01 (AB, J=12.4 Hz, 2H), 2.22–2.20 (m, 1H), 2.08–1.88 (m, 3H), 1.75–1.35 (m, 4H), 1.08–0.94 (m, 6H); MS (75 eV) m/z 290 (M^+, 72), 275 (9), 266 (11), 262 (12), 261 (48), 248 (100), 247 (71), 231 (17), 231 (20), 219 (78), 218 (21), 205 (18), 181 (11), 96 (33), 94 (50).

*4.3.5.3. 1,2b-Dipropyl-2a,2b,8b,8c-tetrahydrocyclopropa[3,4]-pentaleno[1,2-b]quinoxaline (**25**).* ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.06–7.93 (m, 2H), 7.65–7.58 (m, 2H), 5.13 (br, 1H), 3.95 (d, J=8.0 Hz, 1H), 3.32 (t, J=6.0 Hz, 1H), 2.66 (dd, J=4.0, 2.0 Hz, 1H), 2.45–2.35 (m, 2H), 2.30–1.90 (m, 2H), 1.70–1.40 (m, 4H), 0.95 (t, J=7.5 Hz, 3H), 0.85 (t, J=7.4 Hz, 3H).

*4.3.6. Irradiation of **5b***

Following the general procedure, barrelene **5b** with 0.02 M concentration in deuterated benzene afforded **26** in 92% isolated yield. IR (neat) 2947, 2904, 1733, 1716, 1652, 1558, 1507, 1244 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.94–8.00 (m, 2H), 7.66–7.70 (m, 2H), 5.88 (dd, J=2.8, 5.2 Hz, 1H), 5.64 (dd, J=1.0, 5.2 Hz, 1H); 4.76 (dd, J=1.0, 2.8 Hz, 1H), 5.48 (s, 1H), 3.84 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 167.7, 167.2, 160.8, 151.6, 141.6, 140.7, 135.1, 129.6, 129.1, 128.9, 128.8, 123.8, 63.1, 57.9, 55.6, 53.0, 52.7, 45.6; MS (EI, 75 eV) 323 (37) [M^+], 323 (37), 322 (89), 264 (59), 263 (91), 262 (66), 235 (75), 231 (67), 219 (59), 206 (100); HRMS (EI) calcd for $C_{18}H_{14}N_2O_4$ (M^+): 322.0954, found: 322.0942.

*4.3.7. Irradiation of **5c***

Following the general procedure, **5c** (81 mg) in benzene (8 mL) furnished semibullvalenes **27** and **28** with relative yields of 62:38 based on ^1H NMR integrations of the crude products. After removing the solvent in a rotavap, the products were separated in a column (chloroform/ethyl acetate 30:1) to obtain oily liquid of **27** (36 mg, 44%) and **28** (28 mg, 35%), which could not be recrystallized in methanol, hexane, and cyclohexane. Similar results were obtained when **5c** was irradiated using acetone as solvent and sensitizer.

*4.3.7.1. Dimethyl 2b,8b-dipropyl-2b,8b-dihydrocyclopropa[3,4]-pentaleno[1,2-b]quinoxaline-2a,8c-dicarboxylate (**27**).* IR (CCl_4) 3070, 2965, 2940, 2880, 1745, 1640, 1570, 1505, 1470, 1460, 1440, 1380, 1330, 1280, 1215, 1130, 1100, 995, 740 cm^{-1}; UV (CH_3OH) λ_{max}=325.8 nm (7.2×10^3), 246.2 (2.6×10^4), 205.2 (2.1×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.10–8.0 (m, 2H), 7.73–7.63 (m, 2H), 5.63 and 5.40 (AB, J=5.2 Hz, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 2.55–2.45 (m, 2H), 2.45–2.30 (m, 2H), 2.20–2.05 (m, 1H), 1.58–1.50 (m, 1H), 1.50–1.40 (m, 1H), 1.30–1.20 (m, 1H), 1.04 (t, J=7 Hz, 3H), 1.00 (t, J=7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 167.7, 165.9, 161.6, 153.5, 141.6, 140.5, 138.3, 129.5, 128.6, 128.4, 128.2, 122.9, 66.9, 66.3, 58.0, 54.6, 52.3, 51.9, 30.8, 28.3, 21.0, 18.4, 14.7, 14.6; MS (EI, 75 eV) m/z (%) 406 (72) [M^+], 363 (10), 347 (45), 346 (100), 314 (11), 303 (58), 287 (42), 245 (19), 243 (16).

*4.3.7.2. Dimethyl 2b,8b-dipropyl-2a,2b,8b,8c-tetrahydrocyclopropa-[3,4]pentaleno[1,2-b]quinozaline-1,2-dicarboxylate (**28**).* IR (CCl_4) 3070, 3040, 2975, 2940, 2880, 1740, 1735, 1635, 1570, 1505, 1470, 1460, 1440, 1415, 1375, 1350, 1315, 1275, 1250, 1220, 1205, 1165, 1150, 1145, 1115, 1085, 1020, 800, 760, 610 cm^{-1}; UV (CH_3OH) λ_{max}=327.2 nm (7.9×10^3), 246.6 (2.4×10^4), 204.6 (2.4×10^4); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.10–7.92 (m, 2H), 7.72–7.54 (m, 2H), 3.66 (s, 3H), 3.62 (s, 3H), 3.32 and 3.11 (AB, J=6 Hz, 2H), 2.60–1.80 (m, 4H), 1.74–1.32 (m, 4H), 1.04 (t, J=7 Hz, 3H), 0.95 (t, J=7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.5, 162.9, 160.7, 155.3, 148.7, 144.9, 141.9, 140.4, 131.8, 128.8, 128.2, 128.1, 64.6, 54.2, 51.9, 51.8, 45.5, 44.1, 33.7, 31.3, 20.2, 18.4, 14.4, 14.1; MS (EI, 75 eV) m/z (%) 406 (100) [M^+], 391 (5), 377 (13), 364 (35), 363 (23), 347 (56), 347 (60), 346 (22), 332 (37), 303 (34), 290 (21), 245 (20), 231 (12).

*4.3.8. Irradiation of **6a***

Following the general procedure, irradiation of **6a** in deuterated benzene recovered the starting material.

*4.3.9. Irradiation of **6b***

Following the general procedure, barrelene **6b** with 0.02 M concentration in deuterated benzene afforded semibullvalene **29** in 85% isolated yield. Replacement of the solvent with acetone under similar reaction condition afforded **29** in 86% yield.

*4.3.9.1. Dimethyl 2b,10b-dihydrobenzo[g]cyclopropa[3,4]pentaleno-[1,2-b]quinoxaline-2a,10c-dicarboxylate (**29**).* IR (neat) 3055, 2952, 1734, 1654, 1438, 1317, 1247, 1132, 880, 732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.54 (s, 1H), 8.49 (s, 1H), 8.04–8.08 (m, 2H), 7.53–7.57 (m, 2H), 5.89 (dd, J=2.8, 6.0 Hz, 1H), 5.73 (d, J=6.0 Hz, 1H), 4.82 (d, J=2.8 Hz, 1H), 4.56 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 167.6, 167.1, 161.1, 153.1, 138.2, 136.9, 134.6, 133.5, 133.1, 128.3, 128.2, 127.1, 127.0, 126.7, 126.6, 124.6, 62.1, 57.8, 55.7, 52.9, 52.7, 45.4; MS (EI, 75 eV) m/z (%) 373 (27) [M^++H], 372 (100), 313 (67), 312 (58), 285 (35), 269 (37), 255 (44), 254 (80); HRMS (EI) calcd for $C_{22}H_{16}N_2O_4$ (M^+): 372.1110, found: 372.1113.

*4.3.10. Irradiation of **6c***

Benzoquinoxalinobarrelene **6c** (336 mg) in benzene (100 mL) was bubbled with argon for 1 h and irradiated with 350 nm. As checked by ^1H NMR, the reaction was complete after 54 h of irradiation. Based on ^1H NMR integrations, photoproducts **30** and **31** were obtained with relative yields of 59:41. The crude products were further separated by column chromatography using chloroform as eluant. The following fractions were obtained; f1: **30** and **6c** (94 mg); f2: pure **30** (24 mg); f3: pure **31** (112 mg); f4: brownish-viscous liquid. Fraction 4 (f4) was recrystallized in ethanol/hexane to obtain pure **31** (52 mg). Fraction 1 (f1) was purified in a silica gel column with chloroform as eluant to obtain pure **30** (38 mg), and mixture of **30** and **6c** (33 mg). Semibullvalene **31** from f3 and f4 was combined and recrystallized in dichloromethane/hexane to obtain a yellow-green crystal (mp 155–157 °C). Semibullvalene **30** cannot be recrystallized in the same solvent system. Similar results were obtained under sensitized condition.

*4.3.10.1. Dimethyl 2b,10b-dipropyl-2b,10b-dihydrobenzo[g]cyclopropa[3,4]pentaleno[1,2-b]quinoxaline-2a,10c-dicarboxylate (**30**).* IR (CCl_4) 3040, 2960, 2870, 2850, 1750, 1550, 1435, 1260, 1215, 1105, 1075, 1005, 980, 885, 820–730, 630 cm^{-1}; UV (CH_3OH) λ_{max}=372.2 nm (1.7×10^3), 277.4 (9.7×10^3), 233.2 (8.2×10^3); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.54 (s, 1H), 8.49 (s, 1H), 7.99–7.97

(m, 2H), 7.48–7.45 (m, 2H), 5.63 and 5.47 (AB, J=5.2 Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 2.40–2.20 (m, 4H), 2.15–2.02 (m, 1H), 1.50–1.37 (m, 2H), 1.28–1.14 (m, 1H), 0.97 (t, J=8 Hz, 3H), 0.93 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 168.1, 166.4, 162.7, 155.9, 138.8, 138.3, 137.7, 133.5, 133.1, 128.4, 128.2, 127.3, 126.9, 126.5, 126.4, 124.1, 67.1, 65.8, 58.1, 54.4, 52.5, 52.1, 30.9, 28.6, 21.1, 19.9, 15.5, 14.7; MS (EI, 75 eV) m/z (%) 456 (100) [M^+], 427 (15), 424 (13), 413 (22), 397 (49), 396 (55), 389 (11), 367 (15), 365 (16), 353 (36), 337 (25), 295 (18), 246 (15), 231 (10), 86 (24), 84 (51), 44 (53), 31 (35).

*4.3.10.2. Dimethyl 2b,10b-dipropyl-2a,2b,10b,10c-tetrahydrobenzo[g]-cyclopropa[3,4]pentaleno[1,2-b]quinoxaline-1,2-dicarboxylate (**31**).* IR (CCl_4) 3050, 2960, 2930, 2870, 1735, 1550, 1465, 1455, 1435, 1350, 1250, 1215, 1115, 1100, 1070, 1020, 1010, 980, 885, 820–740, 670, 630 cm^{-1}; UV (CH_3OH) λ_{max}=369.6 nm (1.0×10^3), 275.6 (7.1×10^3), 230.0 (4.7×10^3); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.61 (s, 1H), 8.59 (s, 1H), 8.07–8.04 (m, 2H), 7.54–7.52 (m, 2H), 3.68 (s, 3H), 3.65 (s, 3H), 3.32 and 3.12 (AB, J=6.5 Hz, 2H), 2.46–2.34 (m, 2H), 2.21–2.16 (m, 1H), 1.89–1.82 (m, 1H), 1.72–1.48 (m, 4H), 1.06 (t, J=7.4 Hz, 3H), 0.98 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.9, 163.4, 161.9, 157.5, 145.1, 138.9, 137.7, 133.0, 132.8, 128.2, 128.1, 127.7, 127.5, 127.3, 126.6, 126.3, 126.1, 64.9, 53.3, 52.0, 45.3, 44.2, 33.9, 31.4, 20.2, 18.5, 14.5, 14.1; MS (EI, 75 eV) m/z (%) 456 (100) [M^+], 441 (3), 427 (11), 414 (35), 413 (43), 387 (51), 382 (34), 381 (24), 365 (13), 355 (19), 353 (31), 340 (15), 339 (15), 295 (20), 84 (10). Anal. Calcd for $C_{28}H_{28}N_2O_4$: C, 73.66; H, 6.18; N, 6.14. Found: C, 73.72; H, 6.07; N, 6.09.

*4.3.11. Irradiation of **7a***

Benzoquinoxalinobarrelene **7a** (32 mg) in benzene (20 mL) was bubbled with argon for 1 h and irradiated with 350 nm light for 10 h. Based on ^{1}H NMR integrations, photoproducts **32**–**34** were obtained with relative yields of 16:44:40. After removing the solvent under reduced pressure, the crude products were separated in a column using benzene as eluant. Three fractions were obtained: f1 (4 mg, **7a**), f2 (14 mg, mixture of **32**–**34**) and f3 (16 mg, pure **33**). The separation of f2 in a column was repeated but again no separation occurred. We also tried to separate the mixture using HPLC with hexane/ethyl acetate (10:1) as solvent system but only semibullvalene **33** can be separated.

*4.3.11.1. 9b,11a-Dipropyl-9b,9c,9d,11a-tetrahydrodibenzo[f,h]-cyclopropa[3,4]pentaleno[1,2-b]quinoxaline (**32**).* ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.33–9.31 (m, 2H), 9.30–8.58 (m, 2H), 7.76–7.68 (m, 4H), 5.53 (d, J=5.0 Hz, 1H), 5.41–5.40 (m, 1H, dd pattern), 3.13 (d, J=6.2 Hz, 1H), 2.88–2.86 (m, 1H, dd pattern), 2.36–1.52 (m, 8H), 1.09–0.99 (m, 6H).

*4.3.11.2. 9c,11a-Dipropyl-9b,9c,9d,11a-tetrahydrodibenzo[f,h]cyclopropa[3,4]pentaleno[1,2-b]quinozaline (**33**).* IR (neat) 3040, 2960, 2940, 1460, 1420, 1370, 1280, 800, 770, 730 cm^{-1}; UV (CH_3OH) λ_{max}=265.5 nm (2.6×10^4), 254.5 (9.7×10^4); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.20–9.15 (m, 2H), 8.52–8.51 (m, 2H), 7.64–7.59 (m, 4H), 5.47 and 5.16 (AB, J=5.0 Hz, 2H), 3.14 and 2.95 (AB, J=6.2 Hz, 2H), 2.29–2.24 (m, 1H), 2.03–1.94 (m, 2H), 1.61–1.40 (m, 5H), 0.99 (t, J=7.3 Hz, 3H), 0.95 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 163.0, 153.9, 138.7, 137.4, 136.2, 130.7, 130.5, 130.5, 130.3, 128.2, 128.9, 127.2, 127.1, 126.5, 124.9, 124.8, 122.5, 122.5, 64.2, 54.3, 54.3, 40.2, 36.2, 33.1, 21.4, 18.9, 14.8, 14.3; MS (EI, 75 eV) m/z (%) 390 (31) [M^+], 375 (10), 361 (30), 348 (100), 347 (78), 331 (16), 319 (48), 318 (24), 307 (12), 305 (12), 293 (13), 281 (21), 149 (36), 57 (33), 43 (30), 27 (60).

*4.3.11.3. 9b,11-Dipropyl-9b,9c,9d,11a-tetrahydrodibenzo[f,h]cyclopropa[3,4]pentaleno[1,2-b]quinoxaline (**34**).* ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.20–9.15 (m, 2H), 8.53–8.52 (m, 2H), 7.64–7.59 (m, 4H), 5.14–5.13 (br, 1H), 4.02 (d, J=6.1 Hz, 1H), 3.32 (t, J=6.5 Hz, 1H), 3.72 (dd, J=3.3 and 1.1 Hz, 1H), 2.36–1.52 (m, 8H), 1.02 (t, J=7.4 Hz, 3H), 0.84 (t, J=7.4 Hz, 3H).

*4.3.12. Irradiation of **7b***

Following the procedure described in **7a**, benzoquinoxalinobarrelene **7b** (45 mg) in benzene (10 mL) was irradiated for 6 h. Based on ^{1}H NMR integrations the photoproducts **35**–**37** were obtained with relative yields of 42:38:20. The crude products were further separated in a column using benzene as eluant. Four fractions were obtained: f1 (14 mg, **35**), f2 (21 mg, **36** and traces of **35**), f3 (6 mg, mixture of **35** and **36**), and f4 (viscous liquid, mixture of **35** and **36**). Semibullvalene **37** could not be detected after column separation. Similar results were obtained under sensitized conditions with acetone as solvent and sensitizer.

*4.3.12.1. Dimethyl 9b,11a-dipropyl-9b,11a-dihydrodibenzo[f,h]cyclopropa[3,4]pentaleno[1,2-b]quinoxaline-9c,9d-dicarboxylate (**35**).* IR (neat) 3070, 2970, 2880, 1740, 1640, 1610, 1440, 1375, 1330, 1280, 1230, 1200, 1165, 1040, 800, 770, 730 cm^{-1}; UV (CH_3OH) λ_{max}=395.6 nm (1.5×10^4), 374.1 (1.4×10^4), 301.7 (1.2×10^4), 256.1 (4.9×10^4), 202.0 (very large); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.25–9.21 (m, 2H), 8.62–8.60 (m, 2H), 8.57–7.77 (m, 4H), 5.70 and 5.60 (AB, J=5.2 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 2.59–2.33 (m, 4H), 1.66–1.37 (m, 4H), 1.12 (t, J=7.3 Hz, 3H), 1.02 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 168.6, 166.7, 166.6, 160.9, 151.4, 139.7, 139.0, 138.9, 138.8, 131.1, 130.7, 130.2, 130.2, 128.9, 128.8, 127.5, 127.4, 125.3, 122.6, 122.5, 67.5, 67.4, 58.7, 55.9, 52.6, 51.9, 31.2, 28.5, 21.4, 18.7, 15.0 14.9; MS (EI, 75 eV) m/z (%) 506 (70) [M^+], 491 (4), 474 (10), 464 (30), 463 (100), 447 (32), 431 (8), 415 (20), 405 (10), 387 (8), 373 (7), 374 (7), 373 (7), 357 (7), 345 (13), 193 (5), 149 (10), 57 (10), 43 (10), 41 (10).

*4.3.12.2. Dimethyl 9b,11a-dipropyl-9b,9c,9d,11a-tetrahydrodibenzo-[f,h]cyclopropa[3,4]pentaleno[1,2-b]quinoxaline-10,11-dicarboxylate (**36**).* IR (neat) 3080, 3025, 2980, 2970, 2880, 1730, 1610, 1560, 1500, 1460, 1440, 1375, 1280, 1265, 1200, 1170, 1160, 1130, 1075, 1055, 850, 800, 770, 740 cm^{-1}; UV (CH_3OH) λ_{max}=369.8 nm (2.1×10^3), 254.5 (7.9×10^3), 202.0 (very large); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.35–9.23 (m, 2H), 8.63–8.60 (m, 2H), 7.88–7.71 (m, 4H), 3.63 (s, 6H), 3.41 and 3.13 (AB, J=6.5 Hz, 2H), 2.48–3.48 (m, 2H), 2.24–2.00 (m, 2H), 1.98–1.70 (m, 2H), 1.66–1.40 (m, 2H), 1.07–1.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 164.5, 163.7, 159.4, 153.5, 149.8, 145.7, 139.9, 138.5, 131.2, 130.9, 130.6, 130.2, 128.8, 128.6, 127.4, 127.4, 125.1, 124.9, 122.6, 122.6, 65.2, 55.3, 52.0, 51.9, 46.3, 44.6, 34.1, 31.7, 20.7, 18.6, 14.6, 14.4; MS (EI, 75 eV) m/z (%) 506 (100) [M^+], 477 (24), 465 (16), 464 (16), 447 (50), 446 (26), 432 (7), 417 (13), 403 (14), 387 (20), 373 (7), 359 (10), 345 (14), 344 (12), 343 (11), 331 (10), 316 (10), 303 (5), 193 (4), 176 (9), 172 (5), 165 (6), 86 (16), 84 (28), 59 (15), 49 (28).

*4.3.12.3. Dimethyl 9b,11-dipropyl-9b,9c-dihydrodibenzo[f,h]cyclopropa[3,4]pentaleno[1,2-b]quinoxaline-9d,11a-dicarboxylate (**37**).* ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 9.36–9.23 (m, 2H), 8.64–8.6 (m, 2H), 7.88–7.71 (m, 4H), 5.23 (br, 1H), 3.93 (s, 3H), 3.74 (s, 3H), 3.41 (d, J=1.60 Hz, 1H), 2.83–2.84 (m, 2H), 2.20–2.1 (m, 2H), 1.64–1.39 (m, 4H), 1.07–1.03 (m, 6H).

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Supplementary data

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