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Substituent effects on the photorearrangements of unsymmetrically substituted diazinobarrelenes†

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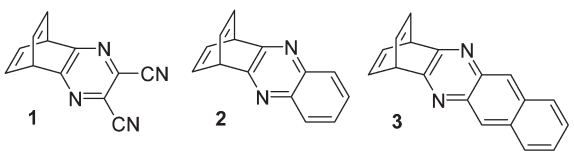
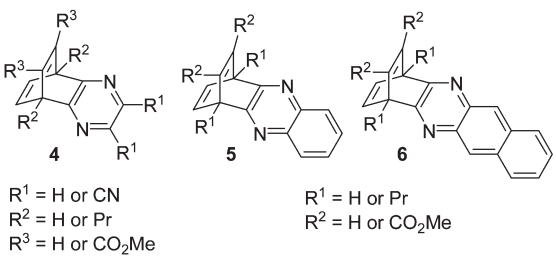
A series of diazinobarrelenes **8–15** engendered with alkyl functionalities at the barrelene skeleton were irradiated with 350 nm light under direct and acetone-sensitized reaction conditions. Under these conditions, all the barrelenes except barrelene **14** afforded semibullvalenes with varying degrees of regioselectivity and product distribution. Dicyanopyrazinobarrelenes **8–10** which furnished semibullvalenes **32–41** *via* the aryl–vinyl initial bridging route were strongly controlled by the nitrile functionalities installed at the aromatic sites. Benzoquinoxalinobarrelenes **11–13** which afforded semibullvalenes **42–49**, preferentially underwent photorearrangement *via* vinyl–vinyl bridging even if the compounds were excited at a wavelength where the quinoxaline moiety absorbed most of the light. Zimmerman's bridging hypothesis and the possibility for quinoxalines to undergo intramolecular triplet energy transfer could reasonably account for the observed regioselectivity. Barrelene **14** was insensitive to photorearrangement whereas benzo[*f*,*h*]quinoxalinobarrelene **15** preferentially underwent ADPM rearrangement affording semibullvalenes **50–52**. Electronic and steric factors of alkyl substituents overwhelmingly controlled the product forming steps whereas localization and minimization of triplet energies greatly influenced the initial bridging interaction.

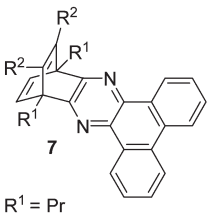
Introduction

Over the past several decades, the photochemical rearrangement of homoconjugated bicyclic systems[1–3] has been shown to be one of the most interesting transformations in the arsenal of organic photochemistry because of its elegant photochemical transformations. The remarkable elaboration of di-π-methane rearrangement (DPM)[1] is one of the most general transformations for these bicyclic systems. Our understanding of this transformation has been acquired from the extensive work of Zimmerman,[1] Paquette,[4] Bender,[5] and Hemetsberger and Nobbe.[6] Much work from these experts has been devoted to the study of substituent effects which can influence reaction rates and impose striking regiospecificity for doubly connected DPM systems such as the barrelenes.[7]



For the past several years, our laboratory has been investigating the photochemical transformations of barrelene analogues such as the pyrazino-, quinoxalino- and benzoquinoxalinobarrelenes[8] wherein the two carbon atoms of the aromatic moiety are replaced by nitrogen. We envisage that the presence of the diazine core which can exhibit both n, π* and π,π* transitions will have a significant influence on the rearrangement of these heteroaromatic barrelenes. In addition, polar and non-polar substituents are installed at strategic sites of the molecules to study the effects of these substituents on regioselectivity during the bridging step of the DPM rearrangement.





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Recently, we reported the results of our investigation on the photochemical transformations of diazinobarrelenes **1–3**.[9] The study indicates that the bridging specificity of these systems is governed by the electronic effect of the nitrile moiety and the triplet energies of the homodiene and diazine moieties during the initial bridging step. Encouraged by these interesting results, we then went on to explore the photochemical behavior of substituted barrelenes **4–6**[10] wherein alkyl, ester, and nitrile substituents are symmetrically attached at the bridgehead, vinylic, and aromatic sites of the bicyclic compounds. In these barrelene analogues, we noticed that similar regioselectivities and product distributions were obtained under direct and sensitized conditions suggesting the efficiency of intersystem crossing (ISC) for these compounds. Factors such as steric and electronic effects and minimization of triplet energy at the reaction surface reasonably account for the observed chemo- and regioselectivity.

In the present work, we disclose the effect of several alkyl substituents which are unsymmetrically installed at the barrelene skeleta of diazinobarrelenes **8–15** (*vide infra*). Conceptually, this kind of installation will lead to photoproducts derived from four possible modes of bridging (Scheme 1) which become intramolecularly competitive. Although an unambiguous demonstration of substituent effects has already been made in some closely related structures such as the benzonorbornadienes[4] and the homoarenebarrelenes,[7a–d] this has never been well demonstrated for diazinobarrelene systems. In pyrazinobarrelenes **8–10**, the nitrile groups at the aromatic site direct the initial aryl–vinyl bridging route of these bicyclic systems whereas in quinoxaline systems **11–13**, vinyl–vinyl bridging is observed despite the localization of the triplet in the aromatic site. Benzoquinoxalinobarrelene **14** is insensitive to photorearrangement. With sufficient triplet energy on the aromatic site, benzo[*f*,*h*]quinoxalinobarrelene **15** furnish semibullvalenes *via* the aryl–vinyl bridging route. In most cases, steric and electronic effects of alkyl substituents greatly influence the product-forming step of the reaction whereas localization of triplet energy controls the initial bridging interaction. Disclosure of the regioselective photorearrangements of dual-channeled heteroaromatic barrelene systems like diazinobarrelenes will be highly informative for future applications.

Results

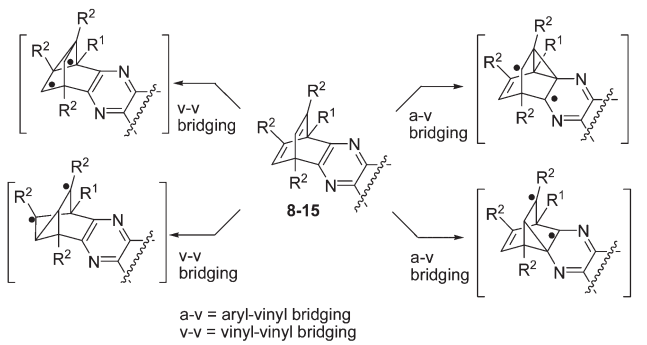
Synthesis of starting materials

In preparing the various diazinobarrelenes **8–15**, we selected the diamines **17–20** to react with diketones **16a–c** by condensation reaction. (Fig. 1) Bicyclo[2.2.2]octadienedione **16a** was easily accessed by oxidation of methoxyphenol **21a**[11a] with diacetoxyiodobenzene (DAIB) in methanol to afford the dimer **22a**[12a] which was then allowed to react with vinylphenyl thioether in sealed tube at 220 °C to give a mixture of constitutional isomers **23a** and **24a** in the ratio of 3 : 1 (4 2). The resulting Diels–Alder (DA) adduct **23a** was subjected to α,β-elimination reaction to obtain dimethoxybicyclic ketone **25a** in 56% yield.[12b] Heating the solution of **25a** in 2 N H_2SO_4 aqueous solution at 70 °C for 12 h afforded the bicyclic diketone **16a** in good yield. Likewise, the five-step reaction sequence as described for **21a** can also be applied for the synthesis of bicylo[2.2.2]octadienedione **16b** using methoxyphenol **21b**[11b] as starting material.

Bicyclo[2.2.2]octadienedione **16c** was obtained from the DA reaction of *tert*-butyl-substituted cyclohexadienedione **28** and *tert*-butyl acetylene **31** at 120 °C for 7 d (Scheme 3). Cyclohexadienedione **28** was easily accessed by subjecting catechol **26** to electrophilic substitution reaction with *t*-BuOH under acidic conditions to afford the alkyl-substituted catechol **27** which was oxidized with HIO_3 to obtain **28** in 94% yield. In the case of acetylene **31**, this was accessed from the chlorination reaction of *tert*-butyl ketone **29** with PCl_5 to afford the dichlorinated alkane **30** which easily underwent successive dehydrohalogenation with *t*-BuOK.

Condensation reactions of bicyclic diketones **16a–c** with 2,3-diaminomaleonitrile (**17**) afforded dicyanopyrazino-barrelenes **8–10**, respectively (Scheme 4) whereas reactions of these diketones with 1,2-diaminoquinoxaline **18** furnished quinoxalinobarrelenes **11–13**, respectively (Scheme 5).

In the cases of benzoquinoxalinobarrelenes **14** and **15**; these were accessed by condensation reactions of bicyclic diketone **16c** in *p*TSA with benzoquinoxaline diamines **19** and **20** under refluxed conditions (eqn (1) and (2)).



Scheme 1 Bridging modes of barrelenes **8–15**.

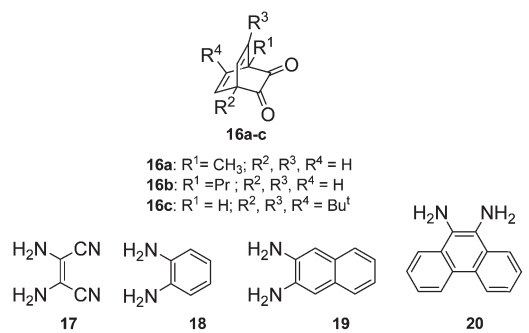
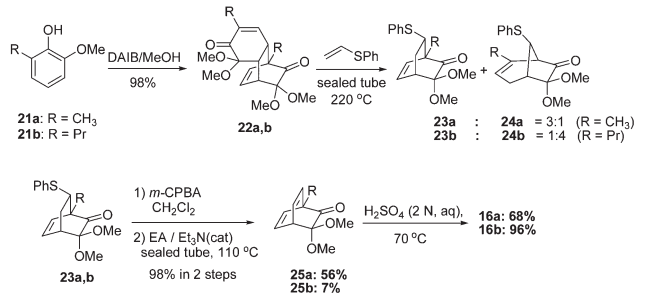
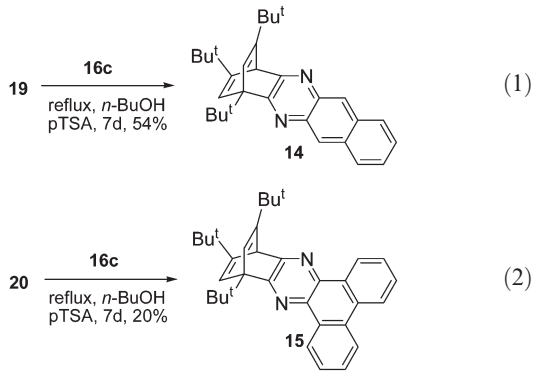


Fig. 1 Diketones **16a–c** and diamines **17–20**.



Scheme 2 Syntheses of bicyclicdienediones **16a** and **16b**.

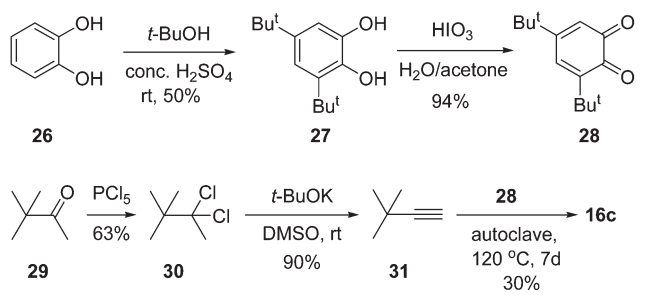


Photorearrangements of diazinobarrelenes 8–15

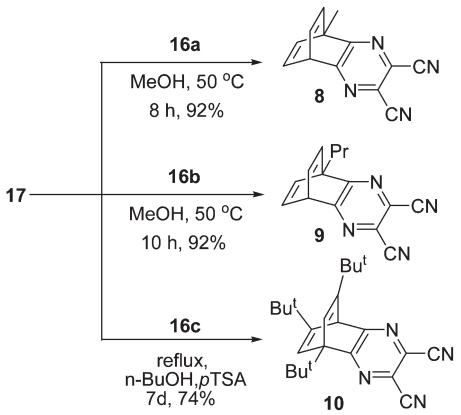
Photorearrangements of diazinobarrelenes **8–15** were performed either on deoxygenated benzene or acetone solutions in Pyrex reaction tubes at room temperature with a broad band of light centered at 350 nm. Consumption of starting materials and generation of photoproducts were monitored by thin-layer chromatography. After the reaction was completed, the solvent was removed *in vacuo* and the photoproducts were immediately determined by ^{1}H NMR spectroscopy. In some cases, the photoproducts were isolated by column chromatography using appropriate eluting solvent systems (see Experimental Section). For non-separable photoproducts, spectroscopic analyses of the mixed photoproducts were sufficient for structural elucidation and quantitative integrations.

Direct photoisomerization of methyl-substituted pyrazinobarrelene **8** in benzene solution afforded four regioisomeric products **32–35** with product distributions ranging from 21–36% as determined by ^{1}H NMR integrations of the reaction mixture (Scheme 6). Semibullvalene **35** could be isolated in pure state. Under triplet-sensitized irradiation of **8** in acetone, the same photoproducts with similar product distributions were obtained. Likewise, the propyl-substituted pyrazinobarrelene **9** either under direct or sensitized irradiations with 350 nm light afforded the regioisomeric photoproducts **36–39** with product distributions ranging from 16–40%. In the case of *tert*-butyl-substituted pyrazinobarrelene **10**, a pair of regioisomeric photoproducts **40** and **41** were generated in 76 : 24 ratio direct irradiation conditions. Interestingly, similar photoproduct distributions were obtained under acetone-sensitized irradiation conditions.

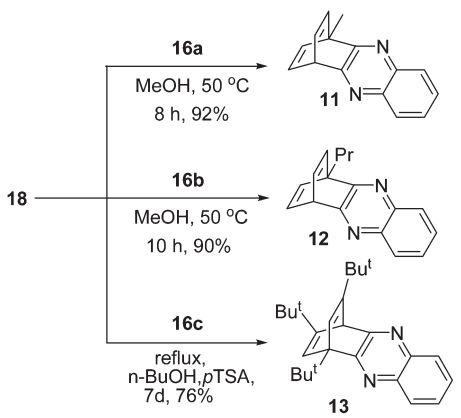
Under direct irradiation of methyl-substituted quinoxalinobarrelene **11** (Scheme 7), the regioisomeric photoproducts **42–44** with relative yields of 33, 56, and 11%, respectively were afforded. Product distributions were determined by ^{1}H NMR integrations; however, the regioisomer **43** could be isolated in pure form. Under acetone-sensitized irradiation of **11**, the same photoproducts were obtained with distributions similar to that obtained under direct irradiation. Unlike the photoisomerization of propyl-substituted pyrazines which generated four regioisomeric products, the propyl-substituted quinoxali-



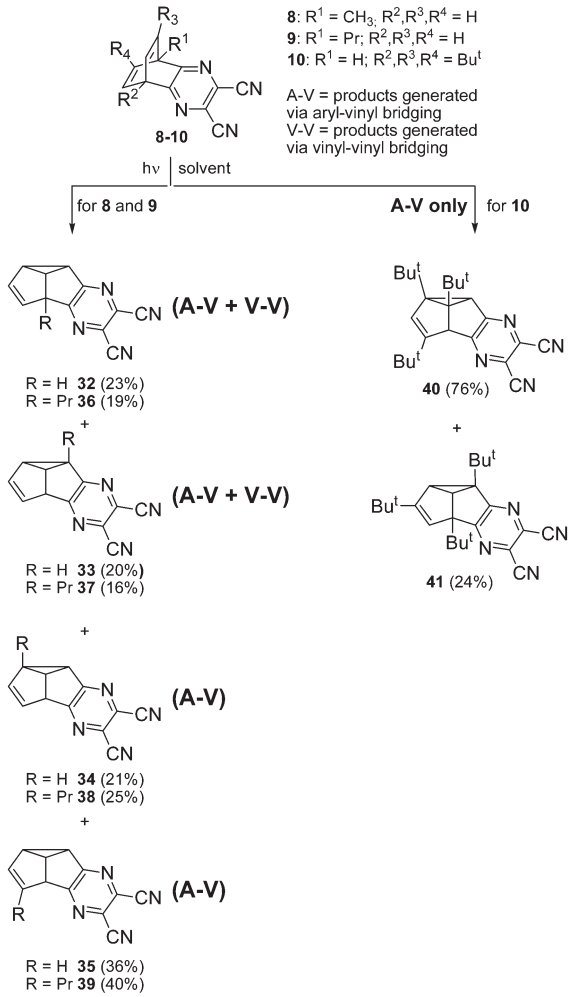
Scheme 3 Synthesis of cyclohexadienedione **28**.



Scheme 4 Syntheses of pyrazinobarrelenes **8–10**.

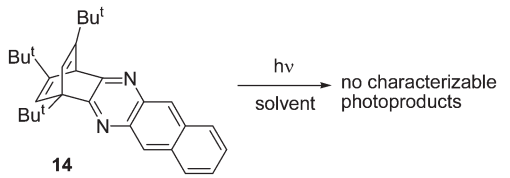


Scheme 5 Syntheses of quinoxalinobarrelenes **11–13**.



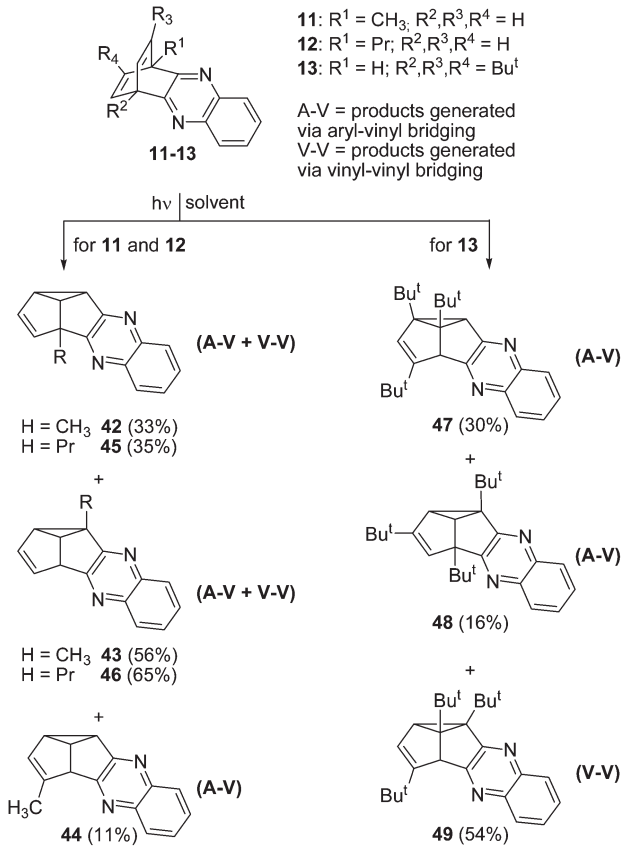
Scheme 6 Photorearrangement of pyrazinobarrelenes **8–10**.

nobarrelene **12** afforded only two photoproducts; the semibullvalenes **45** and **46** with relative yields of 35 and 65%, respectively. In the case of *tert*-butyl-substituted barrelene **13**, the photoproducts **47–49** were obtained in 30, 16, and 54%, respectively. The regioisomeric photoproducts can be obtained either under direct or sensitized irradiation conditions.



(3)

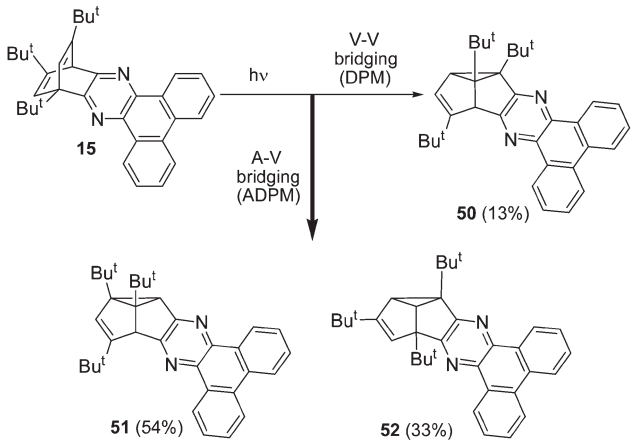
Photoisomerization of benzo[*f*]quinoxalinobarrelene **14** either under direct or sensitized irradiations afforded no characterizable photoproducts (eqn (3)). However, the benzo[*f*,*h*]quinoxalinobarrelene **15** furnished three regioisomeric photoproducts, **50–52** with relative yields of 13, 54, and 33%, respectively (Scheme 8) as determined by ^{1}H NMR integrations. These regioisomers could be isolated in pure state by column chromatography using acetate/hexane (1 : 50) solvent system.



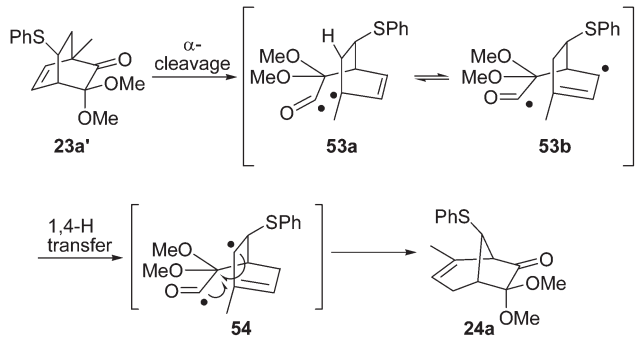
Scheme 7 Photorearrangement of quinoxalinobarrelenes **11–13**.

Discussion

Thermal generation of bicyclo[3.2.1]octadienones **23a,b.** The utility of masked *o*-benzoquinones (MOBs)[13] as precursors of bicyclo[2.2.2]octanones has been extensively studied in our laboratory. We therefore employ this methodology for the synthesis of bicyclo[2.2.2]octadienedione **16a** in a five-step sequence (Scheme 2, *vide supra*). However, during the DA



Scheme 8 Photorearrangement of benzo[*f*,*h*]quinoxalinobarrelene **15**.



Scheme 9 Plausible mechanism for the thermal rearrangement of **23a**′.

reaction of dimer **22a** with phenylvinyl thioether to furnish the bicyclic ketone **23a**, we obtained an interesting side product, the bicyclo[3.2.1]octenone **24a** (*vide infra*). This product could have been generated from the thermal rearrangement of **23a**′, regioisomer of **23a**, through α-cleavage of the bicyclic compound to form the biradical **53a** which then resonated to **53b** and then followed by 1,4-hydrogen transfer[14] to afford the biradical **54** and subsequently collapsed to form the bicyclic octanone **24a** (Scheme 9). The enhanced stability of **53b** which has a secondary carbon radical over that of **53a** which has a tertiary carbon radical may be attributed to the interaction of the sulfide moiety with the secondary radical either by internal coordination or charge-transfer mechanism.[15] This kind of interaction is less likely to be observed from the α-cleavage of **23a**. The structure of **24a** was confirmed from spectroscopic data. (See experimental section) This unprecedented side product from the DA reaction of MOB dimer with vinylphenylthioether could be an alternative route to the synthesis of bicyclo[3.2.1]octanone building blocks.[16] For the synthesis of bicyclic octadienedione **16b** which follows a similar synthetic route as **16a**, a regioisomeric product of **23b** was also observed.

Structural elucidations of photoproducts

The gross structures of methyl-substituted semibullvalenes **32–35**, whose hydrogen atoms are concentrated at the aliphatic sites of the molecules can be distinctively differentiated by ^{1}H NMR spectroscopy (Table 1).

For instance, the vinylic hydrogen chemical shifts of 5.43 (d, 5.43 Hz, 1H) and 5.48 (dd, 2.0, 5.2 Hz, 1 H) along with the cyclopropyl proton chemical shifts of 3.31 (triplet and doublet of triplet) and 3.39 (triplet) ppm and the methyl hydrogen shift at 1.60 ppm fit closely with the gross structure of semibullvalene **32**. The observed δ values for cyclopropyl protons are consistent with the reported values of semibullvalene analogues.[17] Except for the propyl ^{1}H NMR chemical shifts, semibullvalenes **36–39** are shown to have similar spectral patterns like that of **32–35** (See Experimental Section).

In the case of *tert*-butyl-substituted semibullvalenes **40** and **41**, the alkyl proton chemical shifts which can be integrated for 9 H for each *tert*-butyl group are recognizable at δ values close to 1, 1.1, and 1.2 ppm. However, the allyl-, vinyl-, and cyclopropyl hydrogen chemical shifts which appear as singlets at 3.32, 4.28, and 5.49 ppm closely fit the gross structure of semibullvalene **40**. The vinyl proton at 5.12 which is observed as singlet and the cyclopropane hydrogen chemical shifts at 3.18 and 3.20 which appear as an AB system (q, J = 6.4 Hz) are assigned to semibullvalene **41**.

The quinoxalinosemibullvalenes **42–49** were elucidated and the proton spectral features at the fused cyclopentanoid moiety proved almost directly superimposable upon that of the respective pyrazinosemibullvalene **32–41**. Except for the typical spectral profile of the quinoxaline moiety,[18] the spectral features of semibullvalenes **42–44** are comparable to that of semibullvalenes **32**, **33**, and **35**, respectively whereas semibullvalenes **45** and **46** are directly superimposable to that of semibullvalenes **36** and **37**, respectively. In the case of semibullvalenes **47** and **48**, the spectral profiles are comparable to the spectral features of **40** and **41**. In semibullvalene **49**, the distinguishing spectral features are the vinylic proton chemical shift at δ 5.30 which appears as a doublet (J = 2.8 Hz) due to its coupling with the cyclopropyl proton detected at δ 3.0 which also appears as a doublet (J = 2.8 Hz). Except for the typical spectral profile of the benzo[*f*,*h*]quinoxaline moiety,[19] the spectral characteristics of benzoquinoxalinosemibullvalenes **50–52** are directly superimposable to that of semibullvalenes **49**, **47**, and **48**, respectively.

Multiplicities of photorearrangement

Considering the results of this work, one can notice that all the systems (except for benzoquinoxalinobarrelene **14**) undergo either DPM or ADPM rearrangement under direct and sensitized conditions. The typical benzocyclooctatetraene photoproducts which are generated in some homoaromatic barrelene systems[5,7d,24b] during direct irradiation are not observed in our systems which suggest that intersystem crossing from the excited singlet state to the triplet state of these barrelene systems must be very efficient. Pyrazine and quinoxaline are known to have very high ISC quantum yields.[20] This can be attributed to the presence of the lone pair in nitrogen which can enhance the spin–orbit interaction.[21]

Table 1 ^{1}H NMR chemical shifts of the aliphatic protons in **32–35**

Compound	H-1/ppm (*J*/Hz)	H-2/ppm (*J*/Hz)	H-5/ppm (*J*/Hz)	H-6/ppm (*J*/Hz)	H-7/ppm (*J*/Hz)	H-8/ppm (*J*/Hz)
32	3.39, t (5.2)	3.31, t (5.2)	1.60, s (CH_3)	5.43, d (5.2)	5.48, dd (2.0, 5.2)	3.31, dt (2.0, 5.2)
33	3.47, t (6.0)	1.74, s (CH_3)	4.14, dd (2.4, 6.0)	5.64, dd (2.4, 5.2)	5.62, dd (2.4, 5.2)	3.02, dd (2.4, 6.0)
34	3.43, t (6.0)	3.11, d (6.0)	4.16, dd (2.4, 6.0)	5.57, dd (2.4, 4.8)	5.46, d (4.8)	1.66, s (CH_3)
35	3.68, q (6.0)	3.22, dd (6.0, 6.4)	3.90, d (6.0)	32	5.21, m	3.09, ddd (2.4, 6.0, 6.4)

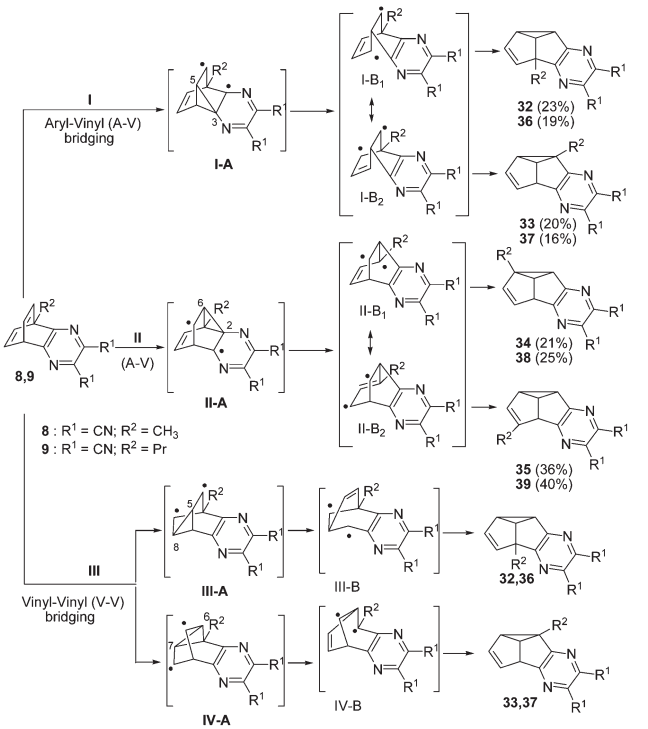
Bridging preferences and photoproduct distributions

Regioselective transformations of barrelenes **8** and **9** are detailed in Scheme 10. In the case of **8**, aryl-vinyl bridging leads to diradical intermediates **I-A** and **II-A**; breaking of the cyclopropyl moieties generates the secondary diradical intermediates **I-B$_1$**, **I-B$_2$** and **II-B$_1$**, **II-B$_2$**, respectively.

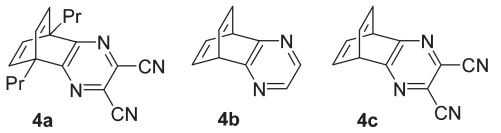
The product-forming step **I-B$_1$** generates semibullvalene **32** whereas **I-B$_2$** furnishes semibullvalene **33**. Closing of diradical in **II-B$_1$** accounts for the photoproduct **34** whereas **II-B$_2$** affords semibullvalene **35**. Initial bridging at the two vinylic moieties generates the cyclopropyldicarbinyldiradical intermediates **III-A** and **IV-A**; breaking of the cyclopropyl moieties affords intermediates **III-B** and **IV-B**, respectively. Closing of these diradicals also furnish the semibullvalenes **32**, **33**, **36**, and **37**. The question arises as to which of the bridging steps (A–V *vs.* V–V bridging) is actually involved in the formation of the aforementioned semibullvalenes. From our previous report on the photorearrangement of dicyano-pyrazinobarrelene **1**[9] and the dipropyl-substituted dicyano-barrelene **4a**,[10] we observed >90% of the photoproducts generated *via* aryl–vinyl bridging. In the case of pyrazinobarrelene **4b**, we observed close to a 1 : 1 ratio of the photoproducts furnished *via* vinyl–vinyl and aryl–vinyl bridging; however, when the nitrile moiety was installed as in **4c** only the photoproduct derived *via* aryl–vinyl bridging was observed.[10] This strongly suggests that the presence of the cyano group is indispensable for the preferred initial bridging.[22] Barrelenes **8** and **9** which have the nitrile groups attached at the pyrazine moiety may have exhibited similar regioselectivity for electron-withdrawing groups are known to lower triplet energies of aromatic compounds,[23] thus the triplet energy is heavily inclined on the aromatic ring.

Zimmerman's bridging hypothesis[7d,24] which considers the energy of the triplet species along the reaction coordinate can also justify the assumption that only aryl–vinyl bridging has occurred in **8** and **9**. In the case of barrelene **8**, as the vinyl group overlaps with the other vinyl moiety, a cisoid butadiene (T_1 = 53.5 kcal mol^{-1})[7d,25] is engendered whereas the bridging of vinyl with dicyanopyrazine group will generate a pyrazinovinyl structure (T_1 = 43 kcal mol^{-1}).[9] From this qualitative approximation, we will expect the triplet energy to be heavily localized in the pyrazine moiety, thus aryl–vinyl bridging is favored. Furthermore, if we are to consider the energies of the initial bridging step which is an energy demanding process, we will expect the aryl–vinyl bridging to be slower than the vinyl–vinyl bridging but then the breaking step of **I-A** and **II-A** to form the second intermediate releases this strain energy of the cyclopropyl moiety and rearomatizes the pyrazine group. This extra stability (rearomatization of pyrazine) which can not be observed in the vinyl–vinyl interaction enhances the observed regioselectivity.

For the photoproduct distributions of **8**, it appears that aryl–vinyl bridging *via* path **II** affords greater yield (57%) than path **I** (43%). The same trend can be observed for pyrazinobarrelene **9** which generates semibullvalenes **38** and **39** in 65% yield *via* path **II** and semibullvalenes **36** and **37** in 35% yield *via* path **I**. The photoproducts of **9** obtained *via* vinyl–vinyl bridging were presumed to be negligible as reasoned out previously. This clearly shows that steric effect of the alkyl substituents installed at the bridgehead position is not considered to be an important factor for the initial bridging process since the bonding occurs at the more hindered side of the barrelene. This kind of phenomenon has been observed in other barrelene systems.[26] The possible influence of the alkyl group for the observed regioselectivity and product distribution could be in the product-forming step. Path **I** generates secondary allylic radicals (**I-B$_1$** and **I-B$_2$**) with no alkyl substituent directly attached to the vinyl moiety whereas path **II** affords a tertiary allyllic radical (**II-B$_1$**) and a secondary allylic radical with alkyl substituent attached at the vinyl moiety (**II-B$_2$**). The alkyl substituents in path **II** stabilize the radical and vinyl moiety through sigma-electron delocalization.[27] One interesting point to notice is the greater relative yield of the photoproducts *via* **II-B$_2$** of which secondary radical is engendered as compared to the photoproducts *via* **II-B$_1$** of which a tertiary radical is engendered. The alkyl group may have imposed some steric effects during the final closing of the diradical to form the product. For instance, the intermediate **II-B$_2$** of **8** wherein the methyl group is not directly attached to the diradical will generate a product such as **35** (36%) which does not have a substituent at the cyclopropyl moiety whereas **II-B$_1$** having a methyl group directly attached at the carbon radical will generate a product such as **34** (21%) which has an alkyl group attached at the cyclopropyl moiety. Interestingly, for the bulkier propyl group installed in **9**, a greater relative yield of **39** (40%) from **II-B$_2$** is obtained as compared to that of **38** (25%) from **II-B$_1$**.

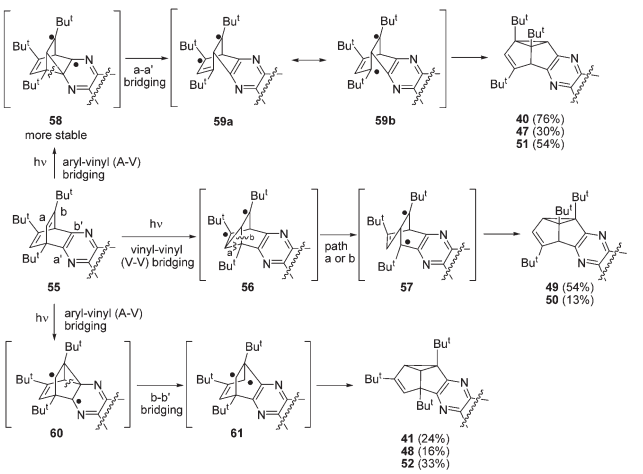


Scheme 10 Plausible mechanism for the photorearrangements of pyrazinobarrelenes **8** and **9**.



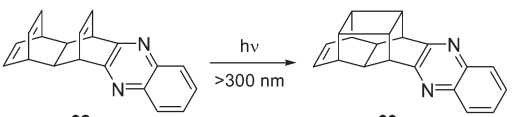
In the case of barrelene **10**, wherein tertiary butyl moieties were installed at the vinylic carbons and in one of the bridge carbons, only aryl–vinyl bridging was observed (Scheme 6, *vide supra*). This result further supports the preferred bridging in **8** and **9** of which photoproducts such as **32** and **33** or **36** and **37** could be generated either by aryl–vinyl or vinyl–vinyl initial bonding interaction. However, the distribution of photoproducts is strongly controlled by the stabilization of radical centers by the tertiary butyl group rather than its steric effect as shown in Scheme 11. Bridging at the a,a′ carbons in **55** furnishes the cyclopropyldicarbinyldiradical intermediate **58** which then breaks to form the more stable diradical intermediates **59a**,**b**. These resonance intermediates generate the semibullvalene **40** in 76% yield whereas aryl–vinyl bonding *via* the b,b′ carbons afford the diradical intermediate **60** which then breaks to form the less stable secondary diradical intermediate **61**. Closing of the diradicals afford the semibullvalene **41** in 24% yield. It is suggested that electron-donating group such as alkyl group attached at the bridge carbon can destabilize the bridging at a,a′ carbon in the same way that electron-donating substituents destabilize the norcaradiene-cyclohepatriene tautomers or the semibullvalene isomers.[28] In addition, steric effect undoubtedly disfavors the formation of intermediate **58** compared to intermediate **60**. But then the initial bonding occurs on this side of the barrelene, thus the stabilization of the tertiary carbon radical in **58** strongly controls the observed regioselectivity.

Quinoxalinobarrelene systems **11–13** exhibit a different product distribution profiles as compared to that of pyrazinobarrelenes **8–10**. In these systems, quinoxalinobarrelene **11** furnishes only three photoproducts; two of these (**42** and **43**) can be generated either by initial aryl–vinyl bridging or by vinyl–vinyl bonding and the other one (**44**) is generated *via* aryl–vinyl bridging. In the case of barrelene **12**, the semibullvalenes **45** and **46** can be generated either *via* aryl–vinyl or vinyl–vinyl bridging. Quinoxalinobarrelene **13**, affords semibullavalenes **47** and **48** with a combined yield of 46% furnished *via* initial aryl–vinyl bridging route and semibullvalene **49** (54%) obtained *via* vinyl–vinyl bonding. The plausible mechanisms of these systems are similar to that of barrelenes **8–10** (Schemes 10 and 11, *vide supra*).



Scheme 11 Plausible mechanisms for the photorearrangements of barrelenes **10**, **13**, and **15**.

The regioselective formation of semibullvalenes **42**, **43**, **45**, and **46** can be traced either *via* aryl–vinyl or vinyl–vinyl bridging. Again, we face the same dilemma as to which of these bridging routes can account for the observed regioselectivity. From our previous report on the initial bridging patterns of deuterated quinoxalinobarrelene **2**[9] and the dipropyl-substituted quinoxalinobarrelene **5** (R^1 = Pr; R^2 = H),[10] vinyl–vinyl bonding was favored. It appears that the same initial bridging pattern can be deduced for barrelenes **11** and **12**. This strong possibility can be justified by analyzing the pattern of product distributions and the plausible mechanisms of the reactions. If we assume that semibullvalenes **42** and **43** were furnished *via* aryl–vinyl bridging, the relative yields of **42** and **43** would have been approximately the same since the product-forming intermediates (**I-B$_1$** and **I-B$_2$**, respectively) have comparable radical stability. This kind of assumption justifies the comparable yields observed in dicyano-substituted semibullvalenes **32** and **33** and in semibullvalenes **36** and **37** wherein A–V bridging was favored. But then the relative yields of semibullvalene **42** and **43** are not similar; in fact semibullvalene **43** is almost twice that of **42**. This kind of product distribution, which is also observed in semibullvalenes **45** and **46**, strongly suggests that the difference in stability of the product-forming intermediates for **42** and **43** is quite large. This differing radical stability of intermediates can easily be noticed in **III-B** and **IV-B**. Semibullvalene **42** which can be generated *via* **III-B** is expected to have a lower yield than **43** which can be generated *via* **IV-B** since the radical centers of the former are both secondary whereas the latter has tertiary radical center. Thus semibullvalenes **42**, **43**, **45** and **46** were furnished *via* vinyl–vinyl bridging route.



(4)

Upon irradiation of quinoxalinobarrelenes **11** and **12** which generate the aforementioned semibullvalenes, light centered at 350 nm was used which essentially perturbs the quinoxaline chromophore; however, photorearrangement took place at the other chromophoric site of the molecule. This indicates that transfer of triplet excitation from the quinoxaline moiety to the homodiene moiety occurred. This possibility is demonstrated by Behr, *et al.*[18] in the phototransformation of benzoquinoxalinobarrelene **62** (eqn (4)) which underwent cycloaddition reaction at the isodrin moiety to form compound **63** although the n,π* and π,π* excitations were localized within the quinoxaline chromophore. Guldi *et al.*[29] has observed that photoexcitation of quinoxaline moiety in the fullerene-qui-

noxaline dyad is followed by rapid intramolecular triplet deactivation of the quinoxaline moiety *via* intramolecular energy transfer to the fullerene moiety. Triplet energy transfer from the quinoxaline moiety (T_1 = 60.6 kcal mol^{-1})[30] to the homodiene moiety (T_1 = 53.5 kcal mol^{-1})[7d,25] in **11** and **12** is feasible based on energetic grounds.

In the case of quinoxalinobarrelene **13**, although vinyl–vinyl bridging is still favored over that of aryl–vinyl bridging, the difference in the yields (54% *vs.* 46%, *vide supra*) of the corresponding semibullvalenes is not really that large. The presence of the bulky-tertiary butyl groups in this barrelene system may have affected the triplet energy transfer through the ''loose bolt'' effect.[31]

Mechanistically, photoproduct distributions of semibullvalenes **42–46** can be explained by odd electron stabilization and partly by steric factors as previously discussed for the photoproduct distributions of semibullvalenes **32–39**. The plausible mechanism presented in Scheme 10 (*vide supra*) is also applicable to this set of barrelene systems. In the case of semibullvalenes **47–49**, distribution of the photoproducts is strongly controlled by the electronic factor. As shown in Scheme 9 (*vide supra*), the relative yields of **47** and **48** is close to 2 : 1. Semibullvalene **47** which is generated *via* a-a′ bonding (Scheme 11, *vide supra*) will furnish the more stable tertiary diradical intermediates **59a**,**b** during the product forming step whereas semibullvalene **48** which is generated *via* b-b′ bridging will afford the less stable secondary diradical intermediate **61**. Photoproduct **49** which is produced *via* vinyl–vinyl bonding also generates the stable tertiary diradical intermediate **57**.

It is interesting to notice that the alkylsubstituted-benzoquinoxalinobarrelene **14** just like the benzoquinoxalinobarrelene[8b,9] previously studied is insensitive to both irradiation conditions (sensitized and direct). However, in Zimmerman's investigation on a closely related anthracenobarrelene[7b] system, DPM rearrangement was observed under direct irradiation but like **14**, no photorearrangement was observed under sensitized conditions. This was explained by invoking the participation of the higher triplet state of anthracenobarrelene which was shown to have a longer lifetime. It is obvious that the enhanced aromaticity of **14** which lowers its triplet energy and the possible involvement of a nitrogen lone pair in spin–orbit interaction hinders the molecule to overcome the energy barrier at the reaction surface.

The dibenzoquinoxalinobarrelene **15** generates photoproduct **50** in 13% yield *via* the vinyl–vinyl bridging route whereas semibullvalenes **51** and **52** with a combined yield of 87% were obtained *via* aryl–vinyl bonding. These results suggest that the initial A–V bonding interaction of **15** has sufficient triplet energy to overcome the energy barrier at the reaction surface. This is expected since the triplet energy of dibenzoquinoxaline (T_1 = 65.7 kcal mol^{-1})[32] is greater compared to the triplet energy of anthracene (T_1 = 43 kcal mol^{-1}).[32] If we are to consider Zimmerman's bridging hypothesis, partial transfer of triplet energy[33] from the heteroarene moiety to the homodiene is strongly favorable. This would account for the formation of the minor photoproduct **50** which is furnished *via* the V–V bridging route.

The formation of semibullvalenes **50–52** can also be explained by considering the stability of radical centers and steric factors. As shown in Scheme 11 (*vide supra*) photoproduct **49** was formed through initial vinyl–vinyl bonding affording the biradical species **56**. The cleavage of either bond **a** or bond **b** of **56** generates symmetrical species **57**; then ring closure occurs to give semibullvalene **50**. Aryl–vinyl bridging *via* a-a′ bonding and b-b′ bonding generate biradical species **59a**,**b** and **61** leading to the formation of semibullvalenes **51** and **52**, respectively. Aryl–vinyl bridging routes (initial a-a′ and b-b′ bridging) predominated over vinyl–vinyl bridging routes due to the stability of the generated biradical species. In addition, owing to steric reasons, a-a′ bonding is more accessible than initial b-b′ bridging and hence the formation of **51** is greater than that of **52**.

Although we have presented a full account of these barrelene systems as regard to their photochemical behaviour and the effect of substituents on regioselectivity, it remains a challenge experimentally on how we could install the nitrile groups on the other barrelene systems and how we could determine triplet energies at the reaction surface so that some of our hypothetical assertions can be fully justified.

Conclusion

We have disclosed the photorearrangements of bicyclo[2.2.2]-diazinobarrelenes **8–15** which are engendered with alkyl and nitrile functionalities. It is very clear that the presence of nitrile functional groups in the heteroaromatic site of the molecule greatly favors the aryl–vinyl initial bridging step as exemplified in the phototransformations of pyrazinobarrelene systems **8–10**. The regioselective transformation of quinoxalinobarrelenes **11–13**, which favor the vinyl–vinyl bridging route, is justified based on Zimmerman's bridging hypothesis and the possibility of quinoxaline systems to undergo intramolecular triplet energy transfer. Benzoquinoxalinobarrelene **14** was insensitive to photorearrangement, which means that the presence of nitrogen greatly influences the deactivation of the triplet state in **14** most likely by spin–orbit interaction. The sufficient triplet energy of the benzo[*f*,*h*]quinoxalinobarrelene **15** on the aromatic site of the molecule greatly influences the observed reactivity and regioselectivity. Although we presented the relative yields of semibullvalenes under direct irradiation with benzene as solvent, we also observed almost the same relative yields when barrelenes **8–15** were irradiated under sensitized conditions. This indicates that the ISC rate for these systems is very efficient. As exemplified in the proposed mechanisms of the reactions, the electronic and steric effects of alkyl substituents are evident in the product-forming steps rather than in the initial-bridging steps. Although product distributions are strongly governed by several structural effects, the key facet of regioselective control and reactivity is greatly influenced by the localization and minimization of triplet energies. However, a full understanding of the photochemical behavior of these barrelene systems will be greatly

appreciated if potential energies at the reaction surface are experimentally accessible.

Experimental section

3,3-Dimethoxy-1-methylbicyclo[2.2.2]octa-5,7-dien-2-one (25a)

MOB dimer **22a** (1.2 g, 7 mmol)**11a** and phenylvinyl sulfide (1.9 g, 14.0 mmol) in toluene (20 mL) were placed in a reaction tube 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 sulfides containing **23a** and **24a** were shown to have relative yields of 75 and 25%, respectively based on ^{1}H NMR integrations. The crude products were separated in a silica gel column (ethyl acetate : hexanes, 1 : 6) to obtain **23a** (711 mg, 2.34 mmol). To a solution of **23a** in CH_2Cl_2 (30 mL), stirred under dry ice bath (−78 °C), was gradually added a solution of mCPBA (576 mg, 2.34 mmol) in CH_2Cl_2 (15 mL). 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 (20 mL) and triethylamine (1 mL) 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 of **25a** (380 mg, 56% yield).

7,7-Dimethoxy-4-methyl-8-(phenylthio)bicyclo[3.2.1]oct-3-en-6-one (24a)

IR (neat): 2944, 2835, 1752, 1583, 1480, 1438, 1141, 1064, 809, 741, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (d, J = 2.0 Hz, 3 H), 2.15–2.20 (br, 1 H), 2.40–2.61 (m, 2 H), 2.89 (dd, J = 2.0, 4.4 Hz, 1 H), 3.31 (s, 3 H), 3.34 (s, 3 H), 3.89 (t, J = 4.4 Hz, 1 H), 5.56 (br, 1 H), 7.21–7.40 (m, 5 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 24.5, 42.2, 45.5, 50.6, 51.5, 54.5, 104.3, 123.9, 126.9, 129.1, 129.8, 131.0, 135.3, 196.2; MS (EI, 70 eV): m/z (%) 304 (0.76) [M$^+$], 276 (16), 245 (4), 213 (3), 167 (100), 135 (10), 91 (11), 75 (27); HRMS (EI): calcd for $C_{17}H_{20}O_3S$: 304.1133, Found: 304.1141.

(25a)

IR (neat): 3063, 2969, 2941, 2834, 1725, 1582, 1457, 1056, 982, 915, 738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 3 H), 3.31 (s, 6 H), 3.94 (tt, J = 6.4, 2.0 Hz, 1H), 6.07 (dd, J = 6.4, 2.0 Hz, 2 H), 6.42 (dd, J = 6.4, 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 43.8, 50.0, 55.8, 90.8, 132.8, 135.0, 196.2; MS (EI, 70 eV) m/z (%): 194 (0.2) [M$^+$], 177 (3), 166 (25), 165 (13), 151 (18), 135 (90), 92 (43), 59 (100); HRMS (EI) calcd for $C_{11}H_{14}O_3$ (M$^+$): 194.0943, Found: 194.0930.

1-Methylbicyclo[2.2.2]octa-5,7-diene-2,3-dione (16a)

A solution of **25a** (380 mg, 1.96 mmol) in 2 N H_2SO_4 (50 mL) was heated at 70 °C while being stirred for 12 h. The reaction mixture was extracted with ether and then the organic layer was washed with water, dried ($MgSO_4$) and solvent was removed under reduced pressure. The crude product was purified by column chromatography (ethyl acetate : hexanes = 1 : 3). After removing the solvent in a rotavap, a yellow crystalline solid of **16a** (197 mg, 68% yield) (mp 64.4–64.7 °C) was obtained. IR (neat): 3069, 2978, 2936, 2876, 1747, 1665, 1453, 1351, 1081, 882, 816, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 (s, 3 H), 4.18 (tt, J = 6.8, 1.6 Hz, 1 H), 6.21 (dd, J = 6.8, 1.6 Hz, 2 H), 6.55 (dd, J = 6.8, 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 51.6, 54.6, 130.1, 136.0, 179.3, 181.7; MS (EI, 70 eV) m/z (%): 148 (0.8) [M$^+$], 93 (8), 92 (89), 91 (100), 77 (5), 65 (18), 63 (9), 62 (4); HRMS (EI) calcd for $C_9H_8O_2$ [M$^+$]: 148.0524, Found: 148.0519.

3,3-Dimethoxy-1-propylbicyclo[2.2.2]octa-5,7-dien-2-one (25b)

Following the procedure described for **25a**, bicyclo[2.2.2]octadienone **25b** was obtained in 7% yield. IR (neat): 3066, 2958, 2925, 2853, 1731, 1465, 1447, 1328, 1146, 1061, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J = 7.2 Hz, 3 H), 1.47 (qt, J = 7.2, 8.0 Hz, 2 H), 1.85 (m, 2 H), 3.30 (s, 3 H), 3.93 (tt, J = 6.4, 2.0 Hz, 1 H), 6.16 (dd, J = 6.4, 2.0 Hz, 2 H), 6.44 (t, J = 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 17.7, 30.6, 43.5, 49.9, 59.6, 91.2, 132.8, 133.0, 196.0; MS (EI, 70 eV) m/z (%): 222 (0.35) [M$^+$], 190 (14), 184 (8), 147 (19), 141 (40), 125 (100), 109 (44), 77 (73).

1-Propylbicyclo[2.2.2]octa-5,7-diene-2,3-dione (16b)

Following the procedure described for **16a**, a solution of **25b** in 2 N H_2SO_4 furnished **16b** in 96% yield. IR (neat): 3066, 2961, 2934, 2872, 1746, 1581, 1466, 1447, 1326, 1146, 1078, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, J = 7.2 Hz, 3 H), 1.50 (qt, J = 7.2, 5.2 Hz, 2 H), 1.95 (m, 2 H), 4.17 (tt, J = 6.4, 2.0 Hz, 1 H), 6.30 (dd, J = 6.4, 2.0 Hz, 2 H), 6.56 (t, J = 6.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 17.4, 29.9, 51.3, 58.3, 130.1, 134.1, 179.8, 181.6; MS (EI, 70 eV) m/z (%): 176 (0.19) [M$^+$], 152 (3), 141 (38), 125 (100), 109 (41), 97 (8), 77 (67), 65 (19).

3,5-Di-*tert*-butylbenzene-1,2-diol (27)

A solution of catechol **26** (100 g, 1.0 mol) in *tert*-butyl alcohol (212 g, 3 mol) was placed in a 1-L reaction flask which was immersed in an ice bath. The mixture was stirred and then concentrated H_2SO_4 (100 mL) was gradually added. The solution was allowed to react for 24 h; water (100 mL) was added and the resulting mixture was extracted with ether (3 ×). The crude product in the organic layer was washed with saturated NaCl, dried ($MgSO_4$) and solvent removed. The gray–white residue was recrystallized from hexane to obtain **27** which is a white crystalline solid (108 g, 50% yield) (mp 96–99 °C). ^{1}H NMR ($CDCl_3$, 90 MHz) δ 6.90 (m, 2 H), 6.74 (m, 2 H), 1.44 (s, 9 H), 1.29 (s, 9 H).

3,5-Di-*tert*-butyl-1,2-benzoquinone (28)

Compound **27** (40 g, 0.18 mol) dissolved in acetone (300 mL) was introduced into a 1 L two-necked flask. A solution of HIO_3 (40 g, 0.22 mol) in water (300 mL) was added gradually with stirring at room temperature for 2 h. After the reaction was complete, the precipitate was isolated by vacuum filtration and then washed with acetone : water solution. The purple–red solid was dried overnight to obtain **28** (37.4 g, 94% yield) (mp 114–115 °C). ^{1}H NMR ($CDCl_3$, 90 MHz) δ 6.92 (d, J = 3 Hz, 1 H), 6.18 (d, J = 3 Hz, 1 H), 1.25 (d, 18 H).

2,2-Dichloro-3,3-dimethylbutane (30)

In a 500 mL reaction flask, PCl_5 (250 g, 1.2 mol) was introduced. Using addition funnel, 3,3-dimethyl-2-butanone (150 mL) was gradually added with stirring at 0 °C for 3 h. The reaction mixture was allowed to react for another 9 h and then 700 g of ice was added to precipitate the product which was then filtered and dissolved in ether. The organic layer was washed with $NaHCO_3$ (10%), dried ($MgSO_4$), and solvent removed to obtain **30** which is a white crystalline solid (118 g, 63% yield).

3,3-Dimethylbut-1-yne (31)

Compound **30** (80 g, 0.52 mol) dissolved in DMSO (40 mL) was introduced in a reaction flask. A solution of *t*-BuOK (120 g, 1.07 mol) in DMSO (200 mL) was gradually added to the reaction mixture with stirring at 40 °C for 2 h. The reaction mixture was subjected to simple distillation at 120 °C and the crude product was collected at 80 °C. The resulting distillate was further separated by fractional distillation at 80 °C to obtain a colorless liquid fraction of **31** (56 mL, 90% yield) which was collected at 38 °C (bp 36.5–38 °C).

1,5,8-Tri-*tert*-butyl-4-methylbicyclo[2.2.2]octa-5,7-diene-2,3-dione (16c)

A mixture of **28** (10 g, 0.045 mol) and **31** (25 mL, 0.205 mol) was placed in a 30 mL high-pressured flask (7 atm) and the reaction was conducted under oil bath at 120 °C for 7 d. The resulting mixture was dissolved in toluene and subjected to fractional distillation to remove the unreacted **31**. After removing the solvent in a rotavap, the residue was purified in a silica gel column (ethyl acetate : hexanes = 1 : 30). A dark-yellow solid was obtained which can be recrystallized from hexane as a light-yellow solid of **16c** (4.1 g, 30% yield) (mp 124–125 °C). IR ($CHCl_3$) 2960, 1735, 1470, 1365, 1240 cm^{-1}; UV (hexane) λ max (ε) = 442.6 (2.6×10^2), 255.3 (2.6×10^3), 197.0 (4.6×10^3); ^1H NMR ($CDCl_3$, 90 MHz) δ 5.96 (d, J = 1.5 Hz, 2 H), 4.21 (t, J = 1.5 Hz, 1 H), 1.70^{-1}. 80 (br, 6 H), 1.25–1.55 (br, 3 H), 1.13 (s, 18 H); MS (EI) m/z (%) 302 (2) [M^+], 246 (22), 232 (21), 231 (95), 108 (6), 94 (6), 57 (53), 55 (8), 43 (8), 41 (18), 29 (16), 18 (100).

General procedures for the syntheses of barrelenes **8–15**. Unless stated otherwise, barrelenes **8**, **9**, **11**, and **12** were synthesized by condensation reaction of the corresponding diamine (1.1 equiv.) and bicyclic octadienedione (1 equiv.) in MeOH at 50 °C for 8–10 h. Solvent was removed from the resulting reaction mixture and the residue was purified in a silica gel column using ethyl acetate : hexanes as eluant. A white crystalline solid was obtained upon recrystallization of the product from dichloromethane or ethyl acetate. Barrelenes **10**, **13**, **14**, and **15** were synthesized by the acid (*p*-TSA) catalyzed reaction of the corresponding diamine (1.4 equiv.) and bicyclic octadiendione (1 equiv.) in BuOH (15 mL) under reflux conditions for 7 d. After solvent workup and purification in a silica gel column, a white solid product was obtained.

5-Methyl-5,8-dihydro-5,8-ethenoquinoxaline-2,3-dicarbonitrile (8)

Diamine **17** (251 mg, 2.37 mmol) in MeOH (15 mL) mixed with bicyclic octadiendione **16a** (318 mg, 2.15 mmol) gave dicyanobarrelene **8** in 92% yield; reaction time = 8 h; column chromatography (ethyl acetate : hexanes = 1 : 2). IR (neat): 3090, 2980, 2937, 2875, 2238, 1612, 1541, 1371, 1341, 1326, 1136, 888, 722 cm^{-1}; UV (MeOH): λ max (ε) = 297 (1.0×10^5); ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 3 H), 5.03 (tt, J = 1.6, 6.0 Hz, 1 H), 6.64 (dd, J = 1.6, 6.0 Hz, 2 H), 7.00 (dd, J = 6.0, 6.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 49.3, 52.9, 113.7, 113.8, 126.2, 126.6, 138.5, 143.4, 163.5, 164.8; MS (EI) m/z (%): 220 (56) [M^+], 219 (100), 205 (24), 194 (11), 92 (9), 90 (10), 62 (16); HRMS (EI) calcd for $C_{13}H_8N_4$ [M^+]: 220.0749, Found: 220.0737; Anal. Calcd for $C_{13}H_8N_4$: C, 70.90; H, 3.66; N, 25.44. Found: C, 71.06; H, 3.36; N, 25.44.

5-Propyl-5,8-dihydro-5,8-ethenoquinoxaline-2,3-dicarbonitrile (9)

Diamine **17** (251 mg, 2.37 mmol) in MeOH (15 mL) mixed with bicyclic octadiendione **16b** (379 mg, 2.15 mmol) gave dicyanobarrelene **9** in 92% yield; reaction time = 10 h; column chromatography (ethyl acetate : hexanes = 1 : 2). IR (neat): 3065, 2961, 2933, 2873, 2236, 1545, 1337, 1146, 1077, 718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, J = 7.2 Hz, 3 H), 1.69 (qt, J = 7.2, 4.4 Hz, 2 H), 2.35 (m, 2 H), 5.00 (tt, J = 6.0, 1.6 Hz, 1 H), 6.73 (dd, J = 6.0, 1.6 Hz, 2 H), 7.01 (t, J = 6.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 18.1, 30.6, 49.0, 56.8, 113.7, 113.8, 126.0, 126.4, 138.5, 141.5, 164.1, 164.9; MS (EI, 70 eV) m/z (%): 248 (36) [M^+], 247 (15), 233 (26), 219 (100), 206 (50), 125 (17), 77 (40); HRMS (EI) calcd for $C_{15}H_{12}N_4$ (M^+): 248.1062, Found: 248.1061.

5,7,9-Tri-*tert*-butyl-5,8-dihydro-5,8-ethenoquinoxaline-2,3-dicarbonitrile (10)

Diaminomaleonitrile **17** (251 mg, 2.37 mmol) in *n*-BuOH (15 mL) mixed with bicyclic octadiendione **16c** (500 mg, 1.65 mmol) and *p*-TSA (158 mg, 0.83 mmol) gave dicyanobarrelene **10** as a white crystalline solid (456 mg, 74% yield) (mp 202–203 °C); time of reaction = 7 d; column chromatography (chloroform : hexanes = 1 : 1). IR ($CHCl_3$) 2960, 2900, 2870, 2240, 1630, 1550, 1465, 1400, 1366, 1330, 1240, 1100, 910, 845 cm^{-1}; UV (*n*-hexane) λ max (ε) = 309.7 (5.0×10^3), 203.1 (1.2×10^4); UV (MeOH) 313.1 (1.0×10^4), 211.7 (2.2×10); ^1H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, J = 2.1 Hz, 2 H), 4.91 (t, J = 2.1 Hz, 1 H), 1.45–1.60 (br, 6 H) 1.15–1.30 (br, 3 H), 1.09 (s, 18 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.1, 166.4, 161.4, 129.8, 125.1, 125.0, 114.1, 114.0, 60.8, 51.7, 35.3, 32.4, 28.5, 25.2; MS (EI, 75 eV) m/z (%) 374 (15) [M^+], 318 (44), 304 (17), 303 (67), 261 (17), 57 (100), 41 (28), 29 (22), 18 (44); Anal. Calcd for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.96; Found C, 76.99; H, 8.19; N, 14.92.

1-Methyl-1,4-dihydro-1,4-ethenophenazine (11)

Diamine **18** (251 mg, 2.32 mmol) in MeOH (15 mL) mixed with bicyclic octadiendione **16a** (312 mg, 2.11 mmol) gave dicyanobarrelene **11** in 92% yield; time of reaction = 8 h; column chromatography (ethyl acetate : hexanes = 1 : 4). IR (neat): 3061, 2973, 2930, 2871, 1620, 1578, 1462, 1356, 1297, 1121, 905, 847, 765 cm^{-1}; UV (MeOH): λ max (ε) = 330 (8.3×10^3), 315 (9.2×10^3), 249 (1.4×10^4); ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3 H), 4.90 (tt, J = 1.6, 6.4 Hz, 1 H), 6.59 (dd, J = 1.6, 6.4 Hz, 2 H), 6.95 (dd, J = 6.4, 6.4 Hz, 2 H), 7.56–7.58 (m, 2 H), 7.81–7.83 (m, 1H), 7.88–7.90 (m, 1 H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 15.8, 49.4, 51.8, 127.9, 128.3, 128.4, 137.3, 137.8, 138.0, 143.1, 158.4, 159.6; MS (EI, 70 eV) *m*/*z* (%): 220 (100) [M^+], 219 (99), 129 (54), 115 (56), 101 (64), 78 (52), 77 (72); HRMS (EI) calcd for $C_{15}H_{12}N_2$ [M^+]: 220.1000, Found: 220.1008; Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.70; H, 5.49; N, 12.72. Found: C, 81.03; H, 5.51; N, 12.73.

1-Propyl-1,4-dihydro-1,4-ethenophenazine (12)

Diamine **18** (251 mg, 2.32 mmol) in MeOH (15 mL) mixed with bicyclic octadiendione **16b** (372 mg, 2.11 mmol) gave dicyanobarrelene **12** in 90% yield; time of reaction = 10 h; column chromatography (ethyl acetate : hexanes = 1 : 4). IR (neat): 3062, 2959, 2932, 2871, 1577, 1460, 1326, 1146, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, J = 7.2 Hz, 3 H), 1.76 (qt, J = 7.2, 4.4 Hz, 2 H), 2.46 (m, 2 H), 4.92 (t, J = 6.4 Hz, 1 H), 6.71 (dd, J = 6.4, 1.6 Hz, 2 H), 6.97 (t, J = 6.4 Hz, 2 H), 7.33 (m, 2 H), 7.82 (m, 1 H), 7.89 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 18.4, 31.2, 49.1, 55.7, 127.9, 128.3, 128.4, 137.2, 137.7, 138.0, 141.1, 159.0, 159.7; MS (EI) *m*/*z* (%): 248 (100) [M^+], 247 (41), 233 (36), 219 (93), 205 (43), 125 (58), 77 (60); HRMS (EI) Calcd for $C_{17}H_{16}N_2$ [M+]: 248.1313, Found: 248.1318.

1,3,11-Tri-*tert*-butyl-1,4-dihydro-1,4-ethenophenazine (13)

Diaminobenzene **18** (251 mg, 2.32 mmol) in *n*-BuOH (15 mL) mixed with bicyclic octadiendione **16c** (500 mg, 1.66 mmol) and *p*-TSA (158 mg, 0.83 mmol) gave dicyanobarrelene **13** as a white crystalline solid (470 mg, 76% yield) (mp 129–130 °C); time of reaction = 7 d; column chromatography (ethyl acetate : hexanes = 1 : 4). IR ($CHCl_3$) 2960, 2900, 2860, 1480, 1470, 1390, 1360, 1305, 1240, 1180, 960, 920, 885, 845 cm^{-1}; UV (*n*-hexane) λ max (ε) = 330.4(6.0 $\times$ 10^3), 316.1 (7.1 $\times$ 10^3) 255.2 (7.3 $\times$ 10^3), 234.1 (8.7 $\times$ 10^3), 215.6 (2.7 $\times$ 10^4); UV (MeOH) 321.2 (9.2 $\times$ 10^3), 236.8 (1.2 $\times$ 10^4), 215.6 (3.6 $\times$ 10^4); ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 18 H), 1.15–1.30 (br, 3 H), 1.55–1.75 (br, 6 H), 4.90 (t, J = 2.1 Hz, 1 H), 6.38 (d, J = 2.1 Hz, 2 H), 7.52–7.55 (m, 2 H), 7.80–7.86 (m, 2 H); ^{13}C NMR (400 MHz,$CDCl_3$) δ 25.3, 28.7, 32.7, 35.2, 51.6, 59.1, 127.7, 127.7, 127.9, 128.7, 129.6, 136.7, 137.1, 160.3, 161.1, 161.7; MS (EI, 75 eV) *m*/*z* (%) 374 [M^+], 318 (40), 317 (72), 304 (19), 303 (68), 261 (56), 248 (21), 247 (24), 86 (19), 84 (28), 59 (33), 57 (36), 43 (100), 41 (28), 29 (19); Anal. Calcd for $C_{26}H_{34}N_2$: C, 83.37; H, 9.15; N, 7.48; Found C, 83.41; H, 9.24; N, 7.57.

1,3,13-Tri-*tert*-*butyl*-1,4-dihydro-1,4-ethenobenzo[b]phenazine (14)

Diaminonaphthalene **19** (366.75 mg, 2.32 mmol) in *n*-BuOH (15 mL) mixed with bicyclic octadiendione **16c** (500 mg, 1.66 mmol) and *p*-TSA (158 mg, 0.83 mmol) gave dicyanobarrelene **14** as a white crystalline solid (450 mg, 64% yield) (mp 256–257 °C). IR ($CHCl_3$) 3080, 3050, 2960, 2900, 2860, 1640, 1600, 1560, 1475, 1460, 1395, 1365, 1320, 1240, 1190, 1080, 1010, 960, 920, 885, 840 cm^{-1}; UV (*n*-hexane) λ max (ε) = 365.3(6.5 $\times$ 10^3), 280.1 (2.1 $\times$ 10^4) 257.5 (3.0 $\times$ 10^4), 238.7 (2.5 $\times$ 10^4), 201.6 (1.1 $\times$ 10^4); UV (MeOH) 368.0 (2.1 $\times$ 10^4), 350.7 (1.8 $\times$ 10^4), 284.2 (5.1 $\times$ 10^4), 258.8 (8. 5 $\times$ 10^4), 237.4 (8.6 $\times$ 10^4); ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 18 H), 1.21–1.33 (br, 3 H), 1.53–1.80 (br, 6 H), 4.89 (t, J = 1.8 Hz, 1 H), 6.37 (d, J = 1.8 Hz, 2 H), 7.44–7.46 (m, 2 H), 7.97–7.99 (m, 2 H), 8.30 (s, 1 H), 8.36 (s, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 25.4, 28.8, 32.7, 35.3, 51.4, 58.7, 125.5, 125.6, 126.5, 128.0, 128.0, 129.0, 133.0, 133.0, 134.8, 135.2, 159.6, 160.3, 160.9; MS (EI, 70 eV) *m*/*z* (%) 424 (14) [M^+], 368 (36), 367 (50), 353 (36), 311 (55), 85 (100), 57 (55), 55 (36), 41 (45), 18 (91) ; Anal. Calcd for $C_{30}H_{36}N_2$: C, 84.85; H, 8.54; N, 6.60; Found C, 84.91; H, 8.64; N, 6.45.

10,12,15-Tri-*tert*-butyl-10,13-dihydro-10,13-ethenodibenzo[*a*,*c*]phenazine (15)

Phenanthrene-9,10-diamine **20** (380 mg, 1.83 mmol) in *n*-BuOH (15 mL) mixed with bicyclic octadiendione **16c** (500 mg, 1.66 mmol) and *p*-TSA (158 mg, 0.83 mmol) gave dicyanobarrelene **15** as a white crystalline solid (160 mg, 20% yield) (mp 235–236 °C). IR ($CHCl_3$) 3080, 2960, 2900, 2860, 1475, 1460, 1385, 1360, 1335, 1240, 1180, 1085, 905, 840 cm^{-1}; UV (*n*-hexane) λ max (ε) = 359.3 (1.2 $\times$ 10^4), 351.4 (5.4 $\times$ 10^3) 342.1 (7.2 $\times$ 10^3), 322.9 (7.0 $\times$ 10^3), 265.2 (2.4 $\times$ 10^4), 257.4 (1.9 $\times$ 10^4), 239.1 (1.8 $\times$ 104), 210.1 (1.5 104), 194.0 (2.3 $\times$ 10^4); UV (MeOH) 359.9 (1.1 $\times$ 10^4), 342.6 (7.5 $\times$ 10^3), 323.1 (7.4 $\times$ 10^3), 265.0 (2.7 $\times$ 10^4), 239.9 (2.0 $\times$ 10^4), 209.7 (1.8 $\times$ 10^4).; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 18 H) ppm, 1.20–1.40 (br, 3 H), 1.63–1.90 (br, 6 H), 5.05 (t, J = 2.1 Hz, 1 H), 6.46 (d, J = 2.1 Hz, 2 H), 7.66–7.73 (m, 4 H), 8.59–8.61 (m, 2 H), 9.12–9.30 (m, 2 H); ^{13}C NMR (400 MHz,$CDCl_3$) δ 25.4, 28.8, 32.8, 35.3, 52.1, 59.8, 122.4, 122.5, 124.8, 124.9, 126.9, 127.1, 127.5, 127.6, 130.2, 130.6, 130.9, 132.4, 161.5, 161.6, 162.7,; MS (EI, 70 eV) *m*/*z* (%) 474 (34) [M^+], 418 (46), 417 (100), 403 (54), 362 (23), 346 (31), 346 (31), 71 (31), 57 (77), 43 (31), 41 (38), 18 (62); Anal. Calcd for $C_{34}H_{38}N_2$: C, 86.03; H, 8.07; N, 5.90; Found C, 85.37; H, 8.18; N, 5.84.

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 performed by column chromatography using ethyl acetate : hexanes as eluant. Unless specified otherwise, relative yields of photoproducts were determined by ^1H NMR integrations of the mixture.

Irradiation of 8.

Irradiation of **8** (10 mg) in C_6D_6 (2 mL) with 350 nm light for 4 h afforded a 23 : 20 : 21 : 36 mixture (determined by ^1H-NMR) of photoproducts **32**, **33**, **34**, and **35**, respectively. The crude mixture was separated in a column (ethyl acetate : hexanes = 1 : 6) to obtain **35** (3.2 mg), and non-separable mixture of **32**, **33**, and **34**.

1-Methyl-2*a*,2*b*,6b,6*c*-Tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]pyrazine-4,5-dicarbonitrile (35)

IR (neat): 3058, 2922, 2854, 2236, 1732, 1626, 1539, 1371, 1332, 972, 836, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76 (d, J = 0.8 Hz, 3 H), 3.09 (ddd, J = 2.4, 6.0, 7.2 Hz, 1 H), 3.22 (dd, J = 6.0, 7.2 Hz, 1 H), 3.67 (ddd, J = 6.0, 6.0, 6.0 Hz, 1 H), 3.90 (d, J = 6.0 Hz, 1 H), 5.21 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 36.2, 41.9, 49.5, 56.3, 113.6, 113.8, 121.7, 129.2, 131.6, 143.9, 157.8, 162.6. MS (EI, 70 eV) *m*/*z* (%): 220 (57) [M^+], 219 (100), 206 (31), 71 (8), 63 (7), 57 (19), 55 (10); HRMS(EI) calcd for $C_{13}H_8N_4$ [M^+]: 220.0749, Found: 220.0770.

Irradiation of 9.

Following the procedure described for **8**, irradiation of **9** furnished photoproducts **36**, **37**, **38** and **39** with relative yields of 19 : 16 : 25 : 40 based on ^{1}H NMR integrations.

Irradiation of 10.

A degassed solution of **10** (100 mg, 0.267 mmol) in benzene (40 mL) afforded **40** (mp 155–156 °C) and **41** (mp 99–100 °C) with relative yields of 76 : 24 based on ^{1}H NMR integrations; time of irradiation = 1.5 h, column chromatography (ethyl acetate : hexanes = 1 : 40).

1,2*a*,6*c*-Tri-*tert*-butyl-2*a*,2*b*,6*b*,6*c*-tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]pyrazine-4,5-dicarbonitrile (40)

IR ($CHCl_3$) 2960, 2900, 2860, 2230, 1630, 1540, 1470, 1400, 1370, 1345, 1240, 860 cm^{-1}; UV (*n*-hexane) λ max (ε) = 289.1 (9.5×10^3), 206.8 (1.5×10^4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 9 H), 1.09 (s, 9 H), 1.22 (s, 9 H), 3.32 (s, 1 H), 4.28 (s, 1 H), 5.49 (s, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 40.0, 60.1, 67.6, 82.7, 113.7, 113.9, 126.1, 127.7, 131.3, 154.4, 160.7, 165.0; MS (EI, 70 eV) *m*/*z* (%) 374 (20) [M$^+$], 318 (18), 317 (13), 262 (15), 261 (19), 57 (100), 41 (30), 29 (20).

2,2*b*,6*b*-Tri-*tert*-butyl-2*a*,2*b*,6*b*,6*c*-tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]pyrazine-4,5-dicarbonitrile (41)

IR ($CHCl_3$) 2960, 2900, 2860, 2240, 1475, 1460, 1390, 1365, 1320, 1240, 1085, 1045, 860 cm^{-1}; UV (*n*-hexane) λ max (ε) = 291.0 (1.4×10^4), 206.8 (1.9×10^4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (s, 9 H), 1.12 (s, 9 H), 1.18 (s, 9 H), 3.20 & 3.18 (q, AB system, J = 6.4 Hz, 2 H), 5.12 (s, 1 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 26.9, 27.9, 28.6, 33.2, 32.3, 33.4, 44.9, 51.9, 52.0, 70.0, 114.1, 114.2, 124.4, 129.2, 129.7, 152.6, 157.9, 164.7; MS (EI, 70 eV) *m*/*z* (%) 374 (18) [M$^+$], 319 (6), 318 (21), 304 (9), 303 (40), 261 (9), 247 (8), 57 (100), 41 (25), 29 (15), 18 (8).

Irradiation of 11.

Following the procedure described for **8**, irradiation of **11** afforded a 33 : 56 : 11 mixture (^{1}H-NMR) of semibullvalenes **42**, **43**, and **44**, respectively. The crude mixture was separated in a column (ethyl acetate/hexanes, 1 : 8) to obtain **43** and non-separable mixture of **42** and **44**.

2*b*-Methyl-2a,2*b*,8*b*,8*c*-tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]quinoxaline (43)

IR (neat): 3059, 2968, 2928, 2870, 1572, 1409, 1059, 833, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3 H), 2.76 (dd, J = 2.4, 6.4 Hz, 1 H), 3.29 (dd, J = 6.4, 6.4 Hz, 1 H), 4.18 (dd, J = 6.4, 2.4 Hz, 1 H), 5.55 (dd, J = 2.4, 4.8 Hz, 1 H), 5.65 (dd J = 2.4, 4.8 Hz, 1 H), 7.58–7.60 (m, 2 H), 7.90–7.92 (m, 1 H), 7.98–8.00 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 40.4, 47.2, 52.3, 52.6, 127.1, 128.2, 128.3, 128.4, 128.6, 133.2, 140.3, 141.8, 157.4, 162.7; MS (EI, 70 eV) *m*/*z* (relative intensity): 220 (64) [M$^+$], 219 (100), 100 (13), 88 (26), 73 (25), 70 (48), 60 (65); HRMS(EI) calcd for $C_{15}H_{12}N_2$ (M$^+$): 220.1000, Found: 220.1013.

Irradiation of 12.

Following the procedure described for **8**, irradiation of **12** furnished semibullvalenes **45** and **46** with relative yields of 35 : 65 based on ^{1}H NMR integrations.

Irradiation of 13.

Following the procedure described for **10**, barrelene **13** furnished semibullvalenes **47**, **48**, and **49** with relative yields of 30 : 16 : 54 based on ^{1}H NMR integrations; time of irradiation = 2.5 h; column chromatography (ethyl acetate : hexanes = 1 : 50).

1,2*a*,8*c*-Tri-*tert*-butyl-2*a*,2*b*,8*b*,8*c*-tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]quinoxaline (47)

IR ($CHCl_3$) 3060, 2960, 2900, 2860, 1460, 1405, 1370, 1320, 1240, 860 cm^{-1}; UV (*n*-hexane) λ max (ε) = 322.9 (1.1×10^4), 246.2 (3.1×10^4), 207.3 (3.8×10^4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 9 H) ppm, 1.09 (s, 9 H), 1.24 (s, 9 H), 3.21 (s, 1 H), 4.36 (s, 1 H), 5.43 (s, 1 H), 7.55–7.58 (m, 2 H), 7.87–7.92 (m, 2 H); ^{13}C NMR (400 MHz,$CDCl_3$) δ 29.5, 30.5, 30.8, 33.7, 33.7, 33.8, 38.8, 60.3, 63.9, 78.1, 124.7, 127.8, 127.9, 128.1, 128.7, 139.5, 141.5, 153.6, 158.9, 164.1; MS (EI, 70 eV) *m*/*z* (%) 374 (35) [M$^+$], 318 (43), 317 (100), 303 (27), 261 (55), 246 (27), 57 (32), 41 (21).

2,2*b*,8*b*-Tri-*tert*-butyl-2*a*,2*b*,8*b*,8*c*-tetrahydrocyclopropa[3,4]pentaleno[1,2-b]quinoxaline (48)

IR ($CHCl_3$) 3060, 2960, 2900, 2860, 1475, 1460, 1390, 1360, 1090, 1045, 850 cm^{-1}; UV (*n*-hexane) λ max (ε) = 326.1 (1.1×10^4), 244.7 (3.1×10^4), 204.5 (3.6×10^4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (s, 9 H), 1.24 (s, 9 H), 1.26 (s, 9 H), 3.04–2.94 (q, 2 H, AB system, J = 6.8 Hz), 5.13 (s, 1 H), 7.54–7.58 (m, 2 H), 7.90–7.96 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 27.2, 28.0, 28.8, 33.0, 33.6, 41.3, 48.4, 49.3, 68.6, 32.7, 125.1, 127.4, 127.7, 128.9, 129.0, 140.0, 140.9, 150.5, 157.0, 164.6,; MS (EI, 70 eV) *m*/*z* (%) 374 (23) [M$^+$], 318 (38), 317 (35), 304 (23), 303 (100), 261 (62), 247 (35), 246 (23), 86 (23), 84 (38), 57 (38), 43 (27), 18 (38).

1,2*b*,8*c*-Tri-*tert*-butyl-2*a*,2*b*,8*b*,8*c*-tetrahydrocyclopropa[3,4]pentaleno[1,2-*b*]quinoxaline (49)

IR ($CHCl_3$) 3060, 2960, 2860, 1475, 1460, 1395, 1365, 1330, 1260, 1235, 1200, 1120, 1065, 1015, 980, 900, 850 cm^{-1}; UV (*n*-hexane) λ max (ε) = 326.1 (1.1×10^4), 246.7 (2.8×10^4), 208.8 (4.0×10^4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9 H), 1.12 (s, 9 H), 1.49 (s, 9 H), 3.00 (d, J = 2.8 Hz, 1 H), 4.41 (s, 1 H), 5.30 (d, J = 2.8 Hz, 1 H), 7.55–7.57 (m, 2 H), 7.86–7.96 (m, 2 H); MS (EI, 70 eV) *m*/*z* (%) 374 (34) [M$^+$], 318 (49), 317 (65), 304 (23), 303 (85), 262 (24), 261 (100), 247 (27), 246 (38), 119 (32), 71 (22), 57 (62), 43 (27), 41 (35), 29 (22), 18 (70).

Irradiation of 15.

Following the procedure described for **10**, barrelene **15** afforded semibullvalenes **50** (mp 207–208 °C), **51** (mp 185–186 °C), and **52** (mp 247–248 °C) with relative yields of 13 : 54 : 33 based on ^{1}H NMR integrations.

9*b*,9*d*,11-Tri-*tert*-butyl-9*b*,9*c*,9*d*,11*a*-tetrahydrodibenzo[*f*,*h*] cyclopropa[3,4]pentaleno[1,2-*b*]quinoxaline (50)

IR ($CHCl_3$) 3060, 2960, 2900, 2860, 1470, 1370, 1270, 1195, 845 cm^{-1}; UV (*n*-hexane) λ max (ε) = 366.9 (1.1×10^4), 349.6 (9.6×10^3), 323.9 (8.5×10^3), 263.4 (3.9×10^4), 255.7 (4.1×10^4), 225.9 (1.9×10^4), 210.7 (1.8×10^4); ^{1}H NMR (400 MHz) δ 1.13 (s, 9 H), 1.16 (s, 9 H), 1.41 (s, 9 H), 3.07 (d, J = 2.8 Hz, 1 H), 4.50 (s, 1 H), 5.26 (d, J = 2.8 Hz, 1H), 7.69–7.72 (m, 4 H), 8.61–8.63 (m, 2 H), 9.16–9.20 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 30.6, 30.9, 31.1, 33.9, 34.1, 34.8, 42.8, 58.9, 59.5, 82.3, 119.6, 122.6, 124.8, 125.0, 127.3, 127.3, 128.1, 130.6, 130.8, 130.8, 130.8, 131.0, 135.5, 138.0, 156.3, 158.8, 160.9; MS (EI, 70 eV) *m*/*z* (%) 474 (34) [M^+], 417 (13), 279 (13), 167 (33), 149 (100), 71 (33), 70 (23), 57 (48), 55 (20), 43 (33), 41 (25) .

9*c*,9*d*,11-Tri-*tert*-butyl-9*b*,9*c*,9*d*,11*a*-tetrahydrodibenzo[*f*,*h*] cyclopropa[3,4]pentaleno[1,2-b]quinoxaline (51)

IR ($CHCl_3$) 3060, 2960, 2900, 2860, 1470, 1450, 1390, 1375, 1260, 1190, 1095, 1040, 1010, 850 cm^{-1}; UV (*n*-hexane) λ max (ε) = 368.0 (2.1×10^4), 350.6 (1.5×10^4), 324.5 (1.2×10^4), 263.4 (5.9×10^4), 255.6 (6.0×10^4), 225.6 (2.5×10^4), 210.4 (2.5×10^4); ^{1}H NMR (400 MHz) δ 9.16–9.29 (m, 2 H), 8.60–8.63 (m, 2 H), 7.69–7.72 (m, 4 H), 5.44 (s, 1 H), 4.45 (s, 1 H), 34.0 (s, 1 H), 1.32 (s, 9 H), 1.18 (s, 9 H), 1.08 (s, 9 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 162.7, 156.5, 154.9, 138.7, 136.4, 130.9, 130.6, 130.4, 128.2, 128.0, 127.2, 124.8, 123.8, 122.6, 122.6, 78.4, 63.7, 60.4, 39.1, 34.0, 33.9, 33.7, 31.0, 30.8, 29.5; MS (EI, 70 eV) *m*/*z* (%) 474, [M^+] 418 (41), 417 (100), 361 (41), 57 (35), 18 (65).

9*b*,10,11*a*-Tri-*tert*-butyl-9*b*,9*c*,9*d*,11*a*-tetrahydrodibenzo [*f*,*h*]cyclopropa[3,4]pentaleno[1,2-b]quinoxaline (52)

IR ($CHCl_3$) 3060, 2960, 2900, 2860, 1470, 1390, 1360, 1095, 1040, 850 cm^{-1}; UV (*n*-hexane) λ max (ε) = 367.0 (1.1×10^4), 349.1 (8.2×10^3), 321.2 (6.9×10^3), 262.9 (3.3×10^4), 255.2 (3.6×10^4), 223.9 (1.2×10^4), 218.0 (1.3×10^4); ^{1}H NMR (400 MHz) δ 0.86 (s, 9 H), 1.35 (s, 9 H), 1.36 (s, 9 H), 3.06–3.11 (q, AB system, J = 6.8 Hz, 2 H), 5.24 (d, J = 2.8 Hz, 1H), 7.69–7.72 (m, 4 H), 8.60–8.62 (m, 2 H), 9.16–9.27 (m, 2 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 27.3, 28.2, 28.8, 32.7, 33.0, 33.6, 41.7, 49.1, 50.1, 69.0, 122.5, 122.6, 125.0, 125.1, 125.6, 127.2, 128.0, 128.1, 130.5, 130.7, 131.0, 131.0, 136.6, 137.5, 149.6, 154.3, 163.0; MS (EI, 70 eV) *m*/*z* (%) 474 (42) [M^+], 418 (42), 417 (100), 361 (90), 346 (35), 57 (60), 41 (30), 18 (45).

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