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PHOTOCHEMISTRY OF PYRAZINO- AND QUINOXALINO-FUSED NAPHTHOBARRELENES[#]

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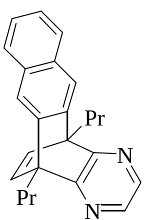
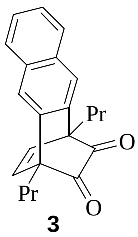
Abstract-Irradiation of the title compounds afforded the corresponding semibullvalenes *via* aza-di-π-methane rearrangement. No naphtho-vinyl bridged products were observed.

Barrelenes undergo facile photoisomerizations to the corresponding cyclooctatetraenes or semibullvalenes based on the irradiation conditions.[1,2] It has been established that cyclooctatetraenes are formed under direct irradiation through a singlet-state pathway involving [2+2] cycloaddition, whereas semibullvalenes are formed upon triplet sensitization through di-π-methane rearrangement (Zimmerman rearrangement).[2] In our earlier papers,[3-6] we reported the photochemistry of pyrazino-, benzopyrazino-, quinoxalino- and benzoquinoxalinobarrelenes. Most of these heteroaromatic barrelenes underwent predominantly aza-di-π-methane (ADPM) rearrangement (heteroaromatic-vinyl bridging) rather than di-π-methane (DPM) rearrangement (vinyl-vinyl bridging or benzo-vinyl bridging). There exists always competition between vinyl-vinyl bridging or benzo-vinyl bridging and heteroaromatic-vinyl bridging i.e. DPM rearrangement and ADPM rearrangement. However, benzopyrazino-[4] and benzoquinoxalinobarrelenes[5] afforded ADPM rearrangement products as the sole or the predominant products based on the substitutions on the heteroaromatic ring. In continuation, we carried out the photochemistry of naphthopyrazino- and naphthoquinoxalinobarrelenes (**1a,b**) and (**2a-c**) with the main aim of examining the competing aptitude of naphthalene and heteroaromatic rings intramolecularly. The propyl groups in compounds (**1a,b**) and (**2a-c**) were designed to be at the bridgehead positions in order to distinguish the possible modes of rearrangement. We herein, report the synthesis and photochemical rearrangement of pyrazino- and quinoxalino-fused naphthobarrelenes (**1a,b**) and (**2a-c**).



1a



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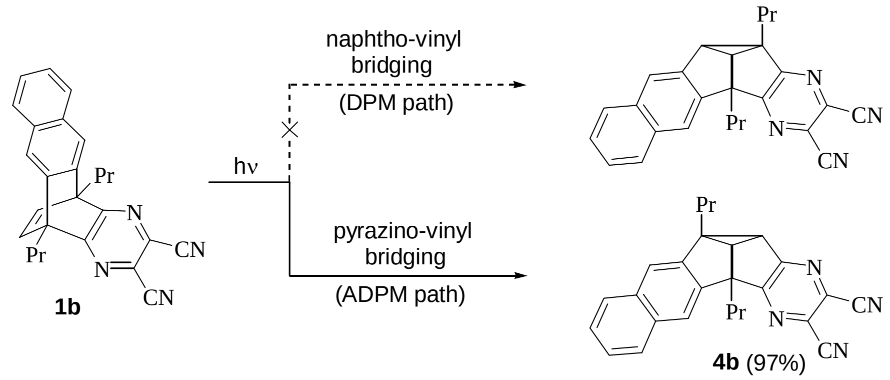
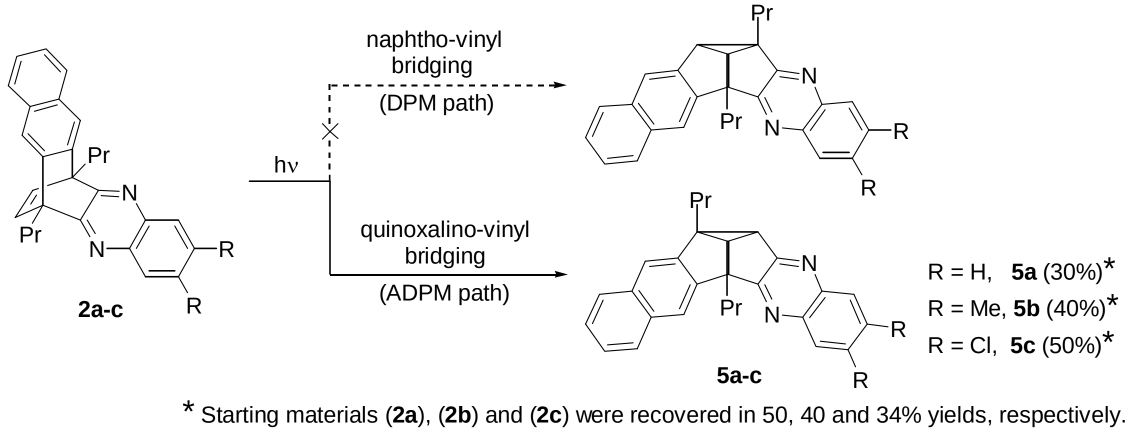
Naphthopyrazinobarrelene (**1a**) was synthesized by the condensation of α-diketone (**3**)[3,7] with ethylenediamine followed by the oxidation with DDQ in 55% yield, whereas naphthobarrelenes (**1b**) and (**2a-c**) were prepared by the condensation of **3** with 1,2-diamino-1,2-dicyanoethylene, 1,2-diaminobenzene, 4,5-dimethyl-1,2-diaminobenzene and 1,2-diamino-4,5-dichlorobenzene in 65, 88, 81 and 81% yields, respectively.

Scheme 1:



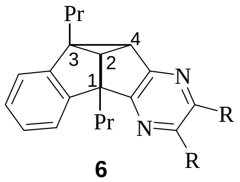
Irradiation of a degassed benzene solution (0.01 M) of **1b** with light of wavelength 350 nm in a Rayonet reactor afforded exclusively the ADPM rearrangement product (**4b**) in 97% isolated yield (Scheme 1). Similarly, irradiation of **2a-c** under the same conditions, resulted in the formation of **5a-c** as the sole products generated *via* ADPM path (Scheme 2). The photochemical reactions of compounds (**1b**) and (**2a-c**) were also performed in perdeuterated benzene in NMR tube and the analysis of ^{1}H NMR (300 MHz) spectra recorded at regular intervals revealed that **4b** and **5a-c**, respectively are the primary photoproducts. Irradiation of **1a** afforded a complex mixture, in which, as shown in its ^{1}H NMR spectrum, neither DPM nor ADPM rearrangement product was observed.

Scheme 2:



* Starting materials (**2a**), (**2b**) and (**2c**) were recovered in 50, 40 and 34% yields, respectively.

The gross structures of naphthopyrazinosemibullvalene (**4b**) and naphthoquinoxalinosemibullvalenes (**5a-c**) were determined from their IR, ^{1}H and ^{13}C NMR, and low- and high-resolution MS spectral analyses. All the photoproducts gave satisfactory elemental analysis. The regiochemistry of the propyl groups was established by comparing their ^{13}C NMR spectral data with those of compounds (**6**), whose structures were established[4,5] earlier in our laboratory. The difference between the chemical shifts of C-3 and C-4 is 9-12 ppm for compounds (**6**) obtained *via* benzo-vinyl bridging (DPM path) and that of C-3' and C-4' is 1-2 ppm for compounds (**7**) obtained *via* heteroaromatic-vinyl bridging (ADPM path). The chemical shift of C-3 (in **6**) is down-field to that of C-3' (in **7**) by at least 4 ppm; whereas the chemical shift of C-4 (in **6**) is up-field to that of C-4' (in **7**) by 4 ppm in all the cases studied. In our present study, the difference between the chemical shifts of C-3 and C-4 for compounds (**4b**) and (**5a-c**) is 9-12 ppm suggesting that their structures are similar to those of compounds (**6**) (Table 1). Thus the assigned regiochemistry for the propyl groups in (**4b**) and (**5a-c**) must come from heteroaromatic-vinyl bridging. The regiochemistry of **4b** was further confirmed from its single crystal X-Ray structure.[8]



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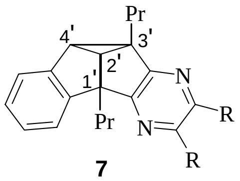

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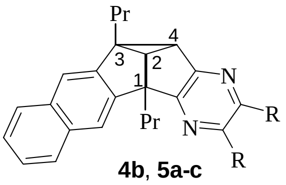


4b, **5a-c**

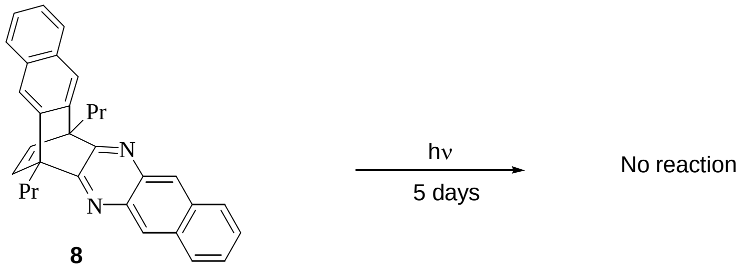
Table 1: Selected NMR data for compounds (**6**), (**7**), (**4b**) and (**5a-c**).[a,b]

Heteroaromatic ring in **6**,**7**, **4b** and **5a-c**	**6** ^{13}C (1-4)	**7** ^{13}C (1'-4')	**4b** and **5a-c**	
			^{13}C (1-4)	^{1}H (mult., *J*)[c]
pyrazine	62.3 (C), 57.8 (CH), 53.6 (C), 41.4 (CH)	61.2 (C), 55.5 (CH), 45.7 (C), 44.0 (CH)		
dicyanopyrazine	61.4 (C), 55.4 (CH), 49.6 (C), 40.6 (CH)		61.9 (C), 56.9 (CH), 52.9 (C), 41.6 (CH)	3.13 and 3.67 (ABq, *J* = 6.0)
quinoxaline	61.5 (C), 54.6 (CH), 50.2 (C), 40.7 (CH)	61.4 (C), 54.9 (CH), 45.6 (C), 44.5 (CH)	61.0 (C), 53.9 (CH), 49.6 (C), 41.0 (CH)	3.15 and 3.55 (ABq, *J* = 6.4)
dimethylquinoxaline	61.4 (C), 54.3 (CH), 49.9 (C), 40.7 (CH)	61.2 (C), 54.6 (CH), 45.6 (C), 44.3 (CH)	61.0 (C), 53.8 (CH), 49.4 (C), 41.4 (CH)	3.12 and 3.52 (ABq, *J* = 6.4)
dichloroquinoxaline	61.5 (C), 54.7 (CH), 50.7 (C), 40.7 (CH)		61.2 (C), 54.2 (CH), 50.3 (C), 41.2 (CH)	3.06 and 3.51 (ABq, *J* = 6.4)

[a] All ^{13}C NMR spectral values are in ppm and the data are presented in the order of C-1, C-2, C-3 and C-4 or C-1', C-2', C-3' and C-4'. [b] The data for the compounds (**6**) and (**7**) are taken from the references 4 and 5. [c] ^{1}H NMR data (in ppm) for cyclopropane ring protons and coupling constants are expressed in Hz; mult. = multiplicity.

The photorearrangements of **1b** and **2a-c** may occur *via* their triplet states, since the same reactions may be sensitized by acetophenone and it is known that pyrazine and quinoxaline undergo more efficient intersystem crossing, (ϕ_{isc} 1.0)[9] and (ϕ_{isc} 0.99),[10] respectively. The formation of **4b** and **5a-c** occurred exclusively *via* pyrazino-vinyl bridging and quinoxalino-vinyl bridging, respectively. Despite the fact that the triplet energy of pyrazine [E_T (n,π*) 75.9 kcal mol^{-1}; E_T (π,π*) 80 kcal mol^{-1}][11] is higher than that of naphthalene [E_T 60.9 kcal mol^{-1}],[12] the reaction of **1b** proceeds only *via* pyrazino-vinyl bridging. This can be explained in terms of the stabilization effect of nitrogen atoms in the pyrazine moiety and the presence of cyano groups through which the reactivity of pyrazino-vinyl bridging is being enhanced.[13] Though the triplet energies of quinoxaline and naphthalene are almost the same ([E_T 60.6 kcal mol^{-1}][14] and [E_T 60.9 kcal mol^{-1}],[12] respectively), the exclusive formation of quinoxalino-vinyl bridged products (**5a-c**) is presumably due to the fact that the presence of nitrogen atoms is known to enhance the rate of the intersystem crossing and to stabilize the radical-like intermediates.[3,4,9,10,15]

It was proposed[16] that the vinyl-vinyl bridging of the DPM rearrangement of 2,3-anthrabarrelene was *via* its upper triplet state (T_2, E_T = 74 kcal mol^{-1}), its lower triplet state (T_1, E_T = 43 kcal mol^{-1}) being inactive. In contrast, compound (**8**) did not undergo a photochemical rearrangement upon prolonged irradiation, which may be due to the upper triplet state being insufficiently long-lived for the chemical reaction (Eq. 1).



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(Eq. 1)

In summary, we have demonstrated that the pyrazino- and quinoxalino-fused naphthobarrelenes undergo the photorearrangement only *via* heteroaromatic-vinyl bridging, rather than naphtho-vinyl bridging. The photochemistry of other heteroaromatic barrelenes is underway in our laboratory.

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Dedicated to Professor Sho Ito on the occasion of his 77th birthday.

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