

# PHOTOCHEMISTRY OF HETEROAROMATIC-RING-FUSED BARRELENES

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The photochemistry of heteroaromatic-ring-fused barrelenes, **6a-b**, **7a-b**, **8a-c**, **9a-c**, and **10a-c**, prepared from the corresponding diketones **1-5** by condensation with 1,2-diamino-1,2-dicyanoethene, 1,2-diaminobenzene, and 2,3-diaminonaphthalene, respectively, were examined to study the substituent effects on their photochemical behavior. Irradiation of a degassed benzene solution of **6a** with UV light centered at 300 nm in a Rayonet reactor afforded a di- $\pi$ -methane (DMP) rearrangement product, **11a** (76%), via heteroaromatic-vinyl bridging and a tri- $\pi$ -methane rearrangement product, **12** (6.7%). Interestingly, no benzo-vinyl bridging product **13a** was found. Irradiation of **10b** gave both **11a** (49%) and **13b** (49%). Irradiation of **8a** and **8b** produced **14a** and **14b**, respectively, derived from DMP rearrangement via a,b-bridging although there are two possible, a,b- and a',b'- heteroaromatic-vinyl, bridgings; the latter process would lead to **15**. For **7a-b** and **9a-b**, recoveries of the starting materials were found after prolonged irradiation. Proton transfers are presumably responsible for no net photochemical reaction in these cases. Irradiation of **10a** furnished **16a** (97%), a heteroaromatic-vinyl bridging product, without the formation of **17a**, a naphtho-vinyl bridging product. Similar result occurred for **10b** to give **16b** (30%). Recoveries of the starting materials were found for **8c** and **10c**. The lowest triplet energies in these cases are presumably too low to cause effective photochemical transformations.