Photorearrangement of some Pyrazinobarrelenes

## Chun-Chen Liao,*[a] Hsing-Pang Hsieh,[a] and Sheng-Yunn Lin[b]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China*
[b] *Department of Chemistry, National Taiwan College of Education, Changhua, Taiwan 50058, Republic of China*

Irradiation of pyrazinobarrelene (1) resulted in di-π-methane rearrangement *via* vinyl–vinyl and pyrazino–vinyl bridges, in the ratio 47 : 53, while irradiation of dicyanopyrazinobarrelenes (2) and (3) afforded only the pyrazino–vinyl bridged products.

The generality of the di-π-methane photorearrangement was first recognized by Zimmerman.[1] In the case of benzobarrelene, direct irradiation in isopentane yielded benzocyclooctatetraene; however, the acetone-sensitized reaction afforded benzosemibullvalene.[2] When deuterium-labelled benzobarrelene was used, it was found that the di-π-methane photorearrangement occurred *via* vinyl–vinyl and benzo–vinyl bridges in the ratio 90 : 10.[2] Recently, Paquette *et al.* reported that the triplet state of the parent 5,8-dihydro-5,8-methanoquinoline underwent di-π-methane rearrangement *via* two possible modes, the major product arising from migration of

the carbon atom *ortho* to the nitrogen atom.[3] They also found that the cyano group showed a profound effect on the regioselectivity of the di-π-methane rearrangement of benzonorbonadienes.[4] We report herein the synthesis and photorearrangement of pyrazinobarrelenes (1), (2), and (3) with the aim of examining the effects of the nitrogen atom and cyano group on the photochemical behaviour of aromatic-fused barrelenes. The propyl groups were designed to be at the bridgehead positions so that the possible modes of rearrangement may be distinguished, while the t-butyl groups were introduced in (3) in order to examine the steric effect.
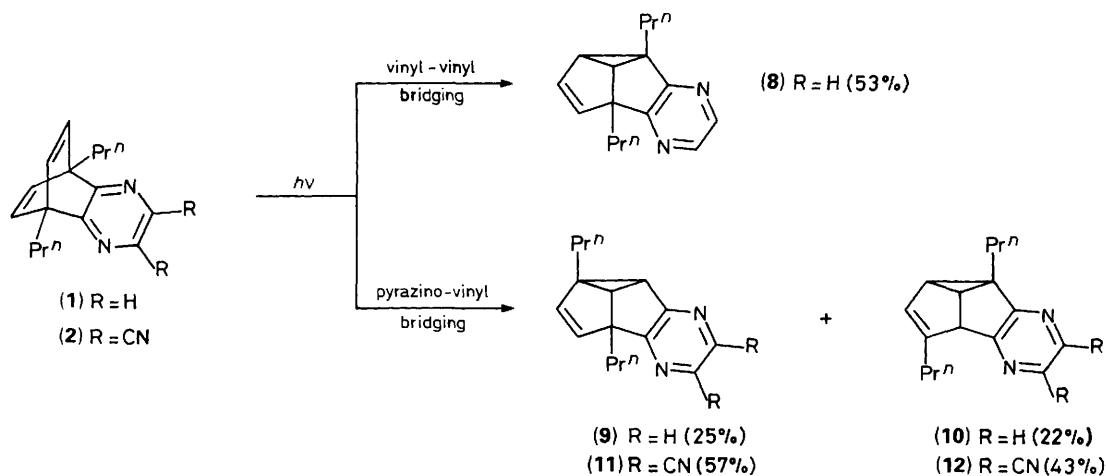
Scheme 1
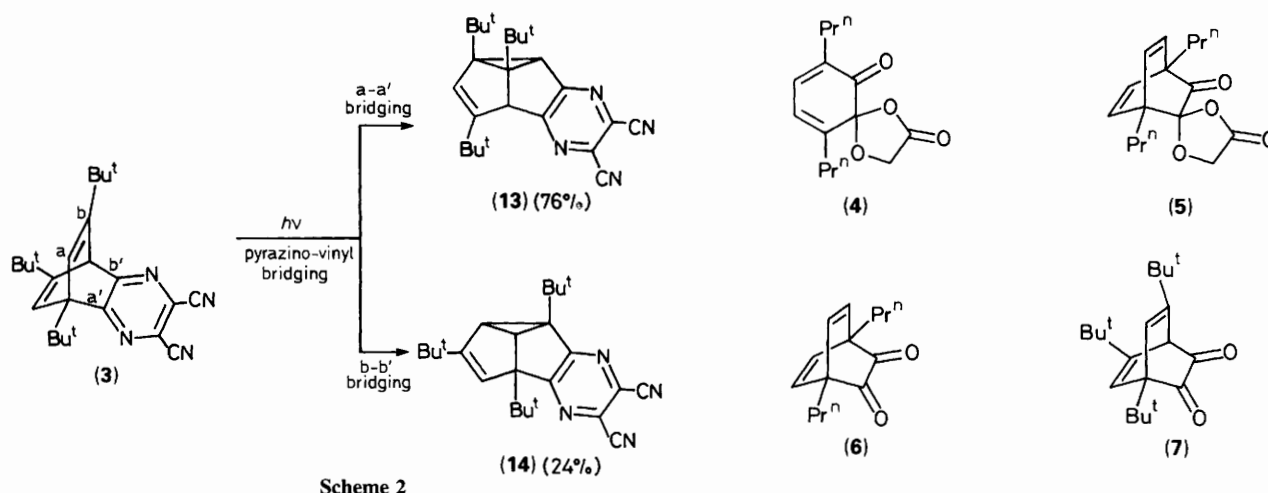
Scheme 2

Compound (1)† was prepared in the following manner. A mixture of masked *o*-benzoquinone (4)[5] and excess phenyl vinyl sulphoxide was heated at 110 °C to give (5), which was presumably derived from *syn* elimination of phenylsulphenic acid[6] from the initially formed Diels–Alder adducts. Alkaline

---

† *Spectroscopic data*, ¹H NMR, for (1): 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). For (2): 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). For (3): δ 6.38 (d, *J* 2.1 Hz, 2H), 4.91 (t, *J* 2.1 Hz, 1H), 1.53 (br. s, 6H), 1.27 (br. s, 3H), 1.09 (s, 18H). For (8): (C₆D₆) δ 7.93 (d, *J* 2.8 Hz, 1H), 7.87 (d, *J* 2.8 Hz, 1H), 5.41 (d, *J* 5.0 Hz, 1H), 5.09 (dd, *J* 5.0, 3.0 Hz), 2.68 (d, *J* 6.2 Hz, 1H), 2.46 (dd, *J* 6.28, 3.0 Hz), 2.34—1.90 (m, 3H), 1.80—1.45 (m, 2H), 1.40—1.27 (m, 3H), 0.92 (t, *J* 6.4 Hz, 6H). For (9): (C₆D₆) δ 8.06 (d, *J* 2.9 Hz, 1H), 7.97 (d, *J* 2.9 Hz, 1H), 5.44 (d, *J* 5.0 Hz, 1H), 5.08 (d, *J* 5.0 Hz, 1H), 2.95 (d, *J* 6.3 Hz, 1H), 2.64 (d, *J* 6.3 Hz, 1H), 2.24—2.19 (m, 1H), 2.06—2.00 (m, 1H), 1.62—1.41 (m, 6H), 1.10 (t, *J* 7.3 Hz, 3H), 0.92 (t, *J* 7.3 Hz, 3H). For (10): (C₆D₆) δ 7.93 and 7.84 (AB system, *J* 2.8 Hz, 2H), 4.90 (d, *J* 1.5 Hz, 1H), 3.66 (d, *J* 6.2 Hz, 1H), 2.81 (t, *J* 6.2 Hz, 1H), 2.36 (dd, *J* 6.2 and 1.5 Hz, 1H), 2.36—1.91 (m, 3H), 1.82—1.46 (m, 2H), 1.40—1.27 (m, 2H), 0.92 (t, *J* 6.4 Hz, 6H). For (11): δ 5.44 (d, *J* 5.0 Hz, 1H), 5.02 (d, *J* 5.0 Hz, 1H), 3.28 (d, *J* 5.8 Hz, 1H), 3.28 (d, *J* 5.8 Hz, 1H), 3.15 (d, *J* 5.8 Hz, 1H), 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). For (12): δ 5.27 (d, *J* 2.4 Hz, 1H), 3.93 (d, *J* 6.4 Hz, 1H), 3.49 (t, *J* 6.4 Hz, 1H), 2.91 (dd, *J* 6.4, 2.4 Hz, 1H), 2.19—1.31 (m, 8H), 0.95 (t, *J* 7.3 Hz, 3H), 0.90 (t, *J* 7.3 Hz, 3H). For (13): δ 5.49 (s, 1H), 4.28 (s, 1H), 3.32 (s, 1H), 1.22 (s, 9H), 1.09 (s, 9H), 0.98 (s, 9H). For (14): δ 5.12 (s, 1H), 3.20 and 3.18 (AB system, *J* 6.4 Hz, 2H), 1.18 (s, 9H), 1.12 (s, 9H), 0.87 (s, 9H). ¹³C NMR for (1): δ 163.7 (s), 142.7 (d), 134.9 (d), 55.8 (s), 31.2 (t), 18.3 (t), 15.0 (q). For (2): δ 166.0 (s), 142.1 (d), 125.8 (s), 113.9 (s), 56.2 (s), 30.6 (t), 18.1 (t), 14.6 (q). For (3): δ 167.1 (s), 166.4 (s), 161.4 (s), 129.8 (d), 125.1 (s), 125.0 (s), 114.1 (s), 114.0 (s), 60.8 (s), 51.7 (d), 35.3 (s), 32.4 (s), 28.5 (q), 25.2 (q). For (11): δ 165.2 (s), 157.5 (s), 134.8 (d), 131.0 (s), 129.4 (s), 128.6 (d), 114.0 (s), 113.7 (s), 64.8 (s), 58.2 (s), 57.3 (d), 41.0 (d), 35.8 (t), 32.2 (t), 21.3 (t), 18.6 (t), 14.4 (q), 14.0 (q). For (12): δ 162.4 (s), 159.5 (s), 148.5 (s), 131.5 (s), 129.0 (s), 121.7 (d), 114.0 (s), 113.9 (s), 54.9 (d), 54.8 (d), 47.9 (d), 47.8 (s), 33.1 (t), 29.3 (t), 20.5 (t), 20.3 (t), 14.2 (q), 13.7 (q). For (13): δ 165.0 (s), 160.7 (s), 154.4 (s), 131.3 (s), 127.7 (s), 126.1 (d), 113.9 (s), 113.7 (s), 82.7 (s), 67.6 (s), 60.1 (d), 40.3 (d), 34.2 (s), 34.0 (s), 33.9 (s), 30.8 (q), 30.5 (q), 29.2 (q). For (14): δ 164.7 (s), 157.9 (s), 152.6 (s), 129.7 (s), 129.2 (s), 124.4 (d), 114.2 (s), 114.1 (s), 70.0 (s), 52.0 (s), 51.9 (d), 44.9 (d), 33.4 (s), 33.2 (s), 32.3 (s), 28.6 (q), 27.9 (q), 26.9 (q). The spectra were taken in CDCl₃ unless otherwise noted.

hydrolysis of (5) gave almost quantitatively α-diketone (6). Biscondensation of (6) with ethylenediamine followed by dehydrogenation with dichlorodicyanoquinone afforded (1) although in low yield (16%). Condensation of (6) and (7) with diaminodicyanoethylene produced (2) and (3)† in 64 and 74% yields, respectively. α-Diketone (7) was prepared by Diels–Alder cycloaddition of 3,5-di-t-butyl-*o*-benzoquinone with t-butylacetylene.

Irradiation of degassed benzene solutions of pyrazino-barrelenes (1), (2), and (3) in a Rayonet reactor (λ 350 nm) afforded clean mixtures of product (Schemes 1 and 2). The yields of the products were based on ¹H NMR (400 MHz) analysis of the irradiated mixtures in degassed deuteriated benzene. The structures of the products were deduced from their spectroscopic (mainly ¹H and ¹³C NMR) data.†

It is interesting to note that, in contrast to benzobarrelene, which undergoes [2 + 2] cycloaddition followed by cycloreversion and electrocyclic transformation to give benzocyclo-octatetraene upon direct irradiation,[2] pyrazinobarrelenes (1), (2), and (3) afford no pyrazinocyclo-octatetraene, from the start of irradiation, as indicated by ¹H NMR analysis of the reaction mixtures. The formation of pyrazinosemibullvalenes upon direct irradiation of (1), (2), and (3) may occur *via* their triplet states, since the same reactions may be sensitized by acetophenone and it is known that pyrazine undergoes more efficient intersystem crossing (φ$_{isc}$ 1.0)[7] than benzene (φ$_{isc}$ 0.23).[8] There are n, π* and π,π* triplet states. It is not clear at the present stage which state is responsible for this di-π-methane rearrangement and whether the vinyl–vinyl and pyrazino–vinyl bridges involve the same triplet state. Nevertheless, in the case of (1), that the pyrazino–vinyl bridging becomes the major reaction pathway may be due to the triplet energy of pyrazine [E_T(n,π*) 75.9 kcal mol⁻¹; E_T(π,π*) 80.0 kcal mol⁻¹][9] being lower than that of benzene (E_T 84.3 kcal mol⁻¹)[10] and the nitrogen atom in the pyrazine moiety enhancing the reactivity of pyrazino–vinyl bridge. The further influence of the cyano groups in (2) and (3) drives the reactions to proceed only *via* pyrazino–vinyl bridging. The preferential formation of (13) (*via* a–a′ bridging) to (14) (*via* b,b′ bridging) may be attributed to the steric effect caused by the t-butyl group at the b position; however, this effect seems to be less profound than that anticipated as reported by Srinivasan and Boyer.[11]

In conclusion, the photochemical behaviour of pyrazino-barrelene and benzobarrelene shows some differences and similarities. The preparation and photochemical studies of other heteroaromatic fused barrelenes are being investigated.

References

1 H. E. Zimmerman, in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 3, pp. 131—166.
2 H. E. Zimmerman, F. S. Givens, and F. M. Pagni, *J. Am. Chem. Soc.*, 1968, **90**, 6096.
3 L. A. Paquette, L. D. Burke, T. Irie, and H. Tanide, *J. Org. Chem.*, 1987, **52**, 3246.
4 L. A. Paquette, D. M. Cottrell, and R. A. Snow, *J. Am. Chem. Soc.*, 1977, **99**, 3723.
5 C. C. Liao and H. S. Lin, *J. Chinese Chem. Soc.*, 1983, **30**, 69.
6 L. A. Paquette, R. E. Moerck, B. Harirchion, and P. D. Magnus, *J. Am. Chem. Soc.*, 1978, **100**, 1597.
7 S. L. Madej, G. D. Gillispie, and E. C. Lim, *Chem. Phys.*, 1978, **32**, 1.
8 R. B. Cundall and L. C. Pereira, *J. Chem. Soc., Faraday Trans.*, 1972, **68**, 1152.
9 B. J. Cohen and J. Goodman, *J. Chem. Phys.*, 1967, **46**, 713.
10 S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973, p. 3.
11 K. G. Srinivasan and J. H. Boyer, *J. Chem. Soc., Chem. Commun.*, 1974, 1026.