

# Unambiguous Proof for Preferred 4 + 4 Cycloaddition in the Dimerization of Photoexcited *N*-Methyl-2-pyridone

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**Summary** Photochemical dimerization of *N*-methyl-2-pyridone in water gives exclusively the 4+4 cycloaddition products *trans-anti* (3) (the known product), *trans-syn* (4), *cis-anti* (5), and *cis-syn* (6a) in yields of 51, 0.6, 11.2, and 6.8%, respectively; structures were assigned on the basis of spectral and chemical evidence.

THE photochemistry of 2-pyridone and its derivatives has been extensively investigated; only the *trans-anti* 4+4 addition product and the valence isomer of the starting material have been obtained, in solutions of high and low concentrations, respectively.<sup>1</sup> In contrast the intramolecular photocycloisomerization of *NN'*-polymethylenebis-2-pyridones has been reported recently to give 2+2, 4+2, and 4+4 addition products.<sup>2</sup> We now report results on the photochemistry of *N*-methyl-2-pyridone.

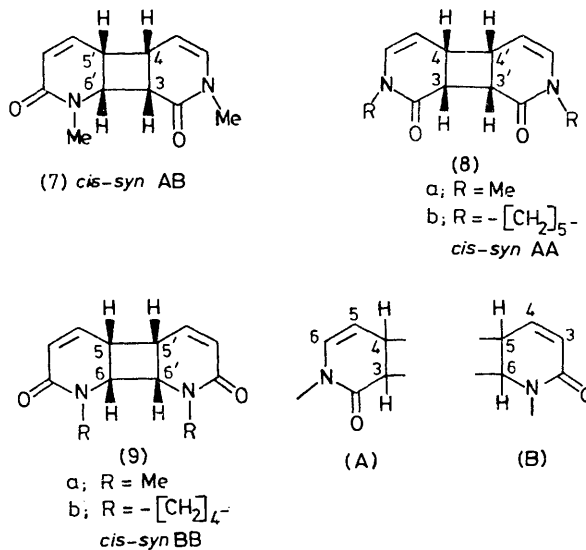
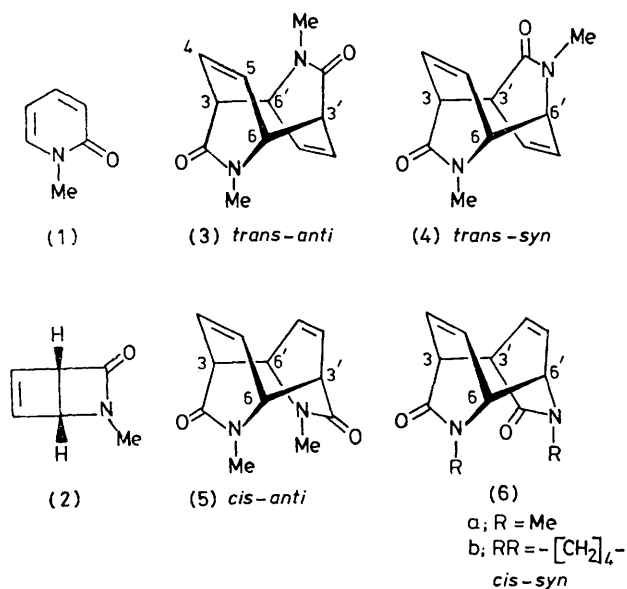
Irradiation (400 W high-pressure mercury arc; Pyrex cell; fine stream of N<sub>2</sub> bubbles; 20 °C; 15 h) of 0.5M aqueous *N*-methyl-2-pyridone (1) gave the known dimer (3) (51%),

TABLE 1. N.m.r. data ( $\delta$  values) for the 4+4 dimers (3)—(6).<sup>a,b</sup> See text for details of double irradiation experiments

	3,3'-H	4,4'-H	5,5'-H	6,6'-H
(3)	3.58	6.17	6.63	3.96
(4)	3.43	6.42	6.42	4.08
(5)	3.63	6.17	6.17	4.10
(6a)	3.60	5.90	6.50	4.08
(6b)	3.62	5.92	6.59	4.06

<sup>a</sup> Recorded in CDCl<sub>3</sub> with Me<sub>4</sub>Si as internal standard, with a JNM-PMX 60 spectrometer. <sup>b</sup> N-Me resonances are in the range  $\delta$  2.75—2.93.

n.m.r. data are in Table 1. They show remarkable differences in their thermal stability; *viz.* (3) and (4) remain unchanged when heated under reflux in CHCl<sub>3</sub> but (5) and (6a) rearrange. Under these conditions, compound (5) rearranged to give only (7), b.p. 110—120 °C at 2.5 × 10<sup>-5</sup> Torr;  $\lambda_{\max}$  262 nm ( $\epsilon$  3210);  $\nu_{\max}$  1665 (C=O) and 1610s cm<sup>-1</sup> (conj. C=C), while (6a) gave (8a), m.p. 141—142 °C;  $\lambda_{\max}$  263 nm ( $\epsilon$  7330);  $\nu_{\max}$  1665 cm<sup>-1</sup> (C=O) and (9a), m.p. 182 °C;  $\lambda_{\max}$  257 nm ( $\epsilon$  2230);  $\nu_{\max}$  1670 (C=O) and 1615s cm<sup>-1</sup> (conj. C=C) in a ratio of 45:55. N.m.r. data for (7)—(9) are in Table 2.



and three new dimers:† (4), m.p. 217 °C (0.6%); (5), m.p. 122—124 °C (11.2%); and (6a), (6.8%) besides a trace of the valence isomer (2) and 19% of recovered (1) after SiO<sub>2</sub> column chromatography. All four dimers showed features characteristic of 4+4 cycloaddition products, having i.r. absorptions at 1655—1660 (C=O) and 1640sh cm<sup>-1</sup> (non-conjugated C=C), and only end u.v. absorptions. Their

In view of the strong similarity between the spectra of (7), (8a), and (9a), and the spectra of the intramolecular cycloaddition products (8b) and (9b),<sup>2</sup> we conclude that (7), (8a), and (9a) have the structures shown; the geometrical

† All new compounds gave satisfactory elemental analyses.

‡ Irradiation of (3)—(6a) separately under the same conditions gave unchanged starting materials, showing that they were photostable. Irradiation at 40 °C under otherwise identical conditions gave further evidence for their photostability; (3) and (4) remained unchanged, (5) changed partly to (7), and (6a) changed partly to (8a) and (9a).

TABLE 2. N.m.r. data for the 2+2 dimers (7)–(9).<sup>a</sup>

	3,4-H <sup>b</sup>	5-H <sup>c</sup>	6-H <sup>d</sup>	3'-H <sup>e</sup>	4'-H <sup>f</sup>	5'-H <sup>b</sup>	6'H <sup>g</sup>
(7)	3.2–3.8	4.77	6.02	5.83	6.40	3.2–3.8	4.2–4.7
(8a)	3.2–3.8	4.87	5.97				
(9a)				5.90	6.27	3.4–3.7	4.2–4.4
(8b)	3.6–4.0	4.3–4.6	6.07				
(9b)				5.92	6.14	3.7–3.9	4.2–4.4

<sup>a</sup> General conditions as in footnote a, Table 1. <sup>b</sup> Multiplet. <sup>c</sup> Multiplet; changes to doublet,  $J$  8 Hz, on irradiation of 3,4-H and/or 5'-H. <sup>d</sup> Doublet,  $J$  8 Hz; changes to singlet on irradiation of 5-H. <sup>e</sup> Doublet,  $J$  10 Hz. <sup>f</sup> Doublet of triplets,  $J$  10 and 2 Hz; changes to broad doublet on irradiation of 3,4-H and/or 5'-H. <sup>g</sup> Multiplet; changes to broad singlet on irradiation of 3,4-H and/or 5'-H.

and steric assignments are based on the following. Compound (7) has an unsymmetrical structure composed of the partial structures (A) and (B); its n.m.r. spectrum shows the C-5 and C-6 vinyl protons of the (A) unit, as in (8b), at  $\delta$  4.77 and 6.02 with coupling between them of 8 Hz. The C-3' and C-4' vinyl protons of the (B) unit, as in (9b), appear at  $\delta$  5.83 and 6.40 with coupling between them of 10 Hz. 4'- and 5-H are further coupled with the cyclobutane protons. The n.m.r. spectra of (8a) and (9a) show that they have symmetrical structures, composed of (AA) and (BB) units, respectively, as shown in Table 2.

Since (7), and (8a) and (9a) were obtained from (5) and (6a), respectively [(5) and (6a) have a Cope system], the double-bond and amide geometries of (5) and (6a) are assigned as *cis-anti* and *cis-syn*, respectively, and the corresponding configurations of (7), (8a), and (9a) as *cis-syn*.<sup>§</sup> The structure assignments are also supported by n.m.r. decoupling experiments. On irradiation of 4,4'; 5,5'-H ( $\delta$  6.17), 3- and 6-H of (5) show further coupling (10 Hz)

with 6'- and 3'-H, while 3- and 6-H of (6a) are coupled only with the olefinic protons 4,4'-H, and 5,5'-H, respectively, as shown by similar irradiation experiments.

Finally, the thermally stable (3) and (4) are similarly assigned *trans-anti* and *trans-syn* structures since 3- and 6-H ( $\delta$  3.58 and 3.96) of (3) are coupled (10 Hz) with 6'- and 3'-H, respectively, whereas 3- and 6-H of (4) appear as singlets at  $\delta$  3.43 and 4.08, respectively, on irradiation of the olefinic protons. The spectral data for (3) agree well with reported data.<sup>1</sup>

In conclusion, the photodimerization of *N*-methyl-2-pyridone gave three new 4+4 cycloaddition products and the known 4+4 product; thus the four possible 4+4 dimers were formed. Other possible 2+2 or 4+2 dimers were not detected.

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<sup>§</sup> *Cis* or *trans* are used to describe the geometry of the double bond and *syn* or *anti* the configuration of the amide in (3)–(6), whereas in (7)–(9) *cis* or *trans* describe the configuration of the cyclobutane ring and *syn* or *anti* the double-bond geometry.

<sup>1</sup> For a review and references, see W. L. Dilling, N. B. Tefertiller, and A. B. Mitchell, *Mol. Photochem.*, 1973, 5, 371.

<sup>2</sup> Y. Nakamura, J. Zindely, and H. Schmid, *Helv. Chim. Acta*, 1976, 59, 2841.