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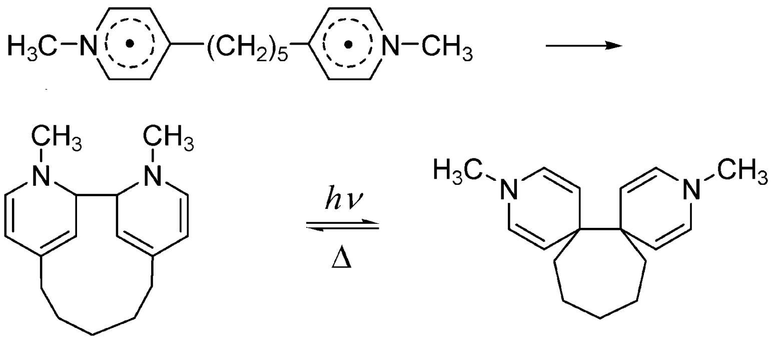

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Visible Light Sensitive Cyclomer and Its Tautomeric Dispiro Compound Formed from Bispyridinyl Diradical

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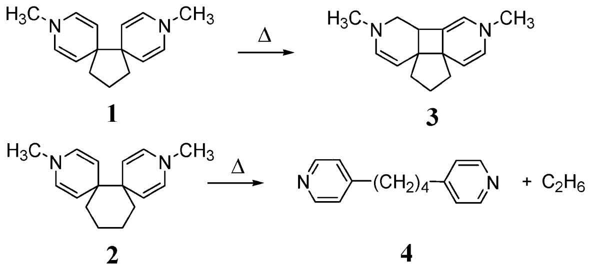
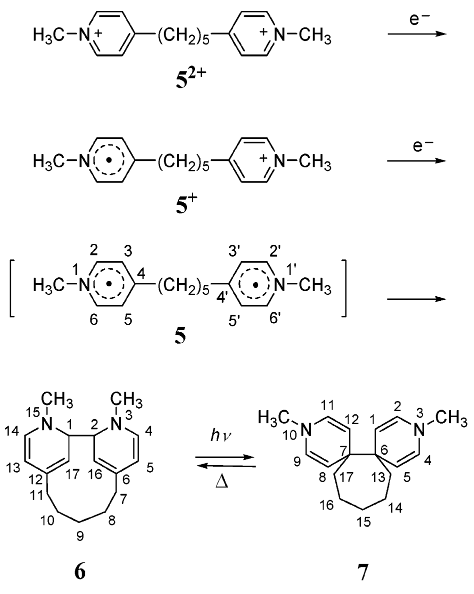
Bispyridiniums of the type Py^+-$(CH)_n$-Py^+ ($Py^+ =$ *N*-methylpyridinium, $n = 3,4$) are promising starting materials for the production of such dispiro compounds as 3,10-dimethyl-3,10-diazadispiro[5.0.5.3]pentadeca-1,4,8,11-tetraene (**1**) and 3,10-dimethyl-3,10-diazadispiro[5.0.5.4]hexadeca-1,4,8,11-tetraene (**2**).[1−3] Interestingly, it was proved that thermal reactivity differs markedly between the two, the former isomerizing to 8,13-dimethyl-8,13-diazatetracyclo[9.4.0.0^{1,5}0.^{5,10}]pentadeca-6,9,14-triene (**3**) and the latter decomposing to 4-(4-(4-pyridyl)butyl)pyridine (**4**). For establishing the chemistry of dispiro compounds through systematic studies of physicochemical properties,[4] we attempted here to prepare a higher homologue of **2**. Contrary to our expectation, however, since two-electron reduction of 4,4′-(1,5-pentanediyl)bis(*N*-methylpyridinium) (**5**$^{2+}$) led to the formation of a cyclomer containing an 11-membered ring,[5,6] we report herein its property together with the photoreaction product.



1 **3** **2** **4**

By the use of standard vacuum-line techniques,[7] reduction of **5**$^{2+}$ was carried out in the dark with sodium amalgam in degassed acetonitrile. The reduction process was followed by means of UV−vis absorption and EPR spectroscopy. The spectral changes during the course of reduction are as follows. Before reduction, a solution of **5**$^{2+}$ exhibits the longest wavelength absorption maximum at 315 nm. After about 30 min of reduction, a weak EPR spectrum due to a radical species was detected that displayed a well-resolved hyperfine structure.[8] The EPR spectrum was interpreted as arising from the 1-methyl-4-[5-(1-methyl(4-pyridyl))pentyl]pyridine cation radical (**5**$^{+}$).[9] After 1 h of reduction, no traces of EPR signals were detected at all. Note, however, that **5**$^{+}$ is stable for a long period of time in a sealed tube under vacuum in Na−Hg-free solution at room temperature. After 5 h of reduction, the spectrum exhibited an absorption maximum at about 350 nm and a long absorption tailing spread over the visible region up to 460 nm. Upon further reduction, neither absorption spectral change nor an EPR spectrum was observed at all. Accordingly, it can be concluded that **5**$^{2+}$ should undergo two sequential one-electron reductions to give diamagnetic species.

Since the reduction products are unstable to air oxygen,[10a] the characterization was carried out in a sealed tube under vacuum. Obviously, the ^{1}H NMR spectrum reveals that the chief product should have a symmetric structure because the spectral features of the major component are quite simple.[10b] The signals observed at the region of 4.52−5.69 ppm were assigned as arising from the protons of dihydropyridine rings. A clear correlation was found to exist between the proton assignments obtained by means of the spin-decoupling and H,H COSY techniques, indicating the formation of a single cyclomer as the chief product. Consequently, the structural assignment was made reasonably such that the product should possess the structure of 2,2′-cyclomer, 3,15-dimethyl-3,15-diazatricyclo[10.3.1.1^{2,6}]heptadeca-4,6(16),12(17),13-tetraene (**6**) (Table 1). In short, **6** is characterized by a structurally novel tricyclic compound containing an 11-membered ring formed from the 4,4′-(1,5-pentanediyl)bis(*N*-methylpyridinyl) diradical (**5**) by intramolecular cyclization.[11] The formation of **6** is notable in view of the facts that the two-electron reduction of the lower bispyridiniums affords the dispiro compounds. This aspect will be interpreted in terms of a thermodynamic stability. Full geometry optimizations by the AM1 method reveal that 3,15-diazatricyclo[10.3.1.1^{2,6}]-heptadeca-4,6(16),12(17),13-tetraene, the parent of **6** is about 10 kcal/mol lower in energy than the valence isomeric dispiro compound, i.e. the 4,4′-cyclomer containing a seven-membered ring.[12]



5^{2+} **5**$^{+}$ **5** **6** **7**

Under degassed conditions, **6** is stable for a long period of time at room temperature. In contrast, the photochemical reaction takes place when **6** is irradiated with light of wavelength about 310−420 nm,[13] whereby the acetonitrile solution changes from a light yellow to a light orange color. Thus far, it has not been known that cyclomers containing no conjugated chromophores respond to

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Table 1. 400 MHz NMR Data of **6** and **7**[a]

^{13}C NMR		^{1}H NMR			^{13}C NMR		^{1}H NMR		
position	δ/ppm	δ/ppm		J/Hz	position	δ/ppm	δ/ppm		J/Hz
	6					**7**			
1, 2	64.36	3.83	d	4.40	1, 5, 8, 12	104.45	4.72	d	8.30
4, 14	136.93	5.69	d	7.32	2, 4, 9, 11	129.46	5.70	d	8.30
5, 13	108.08	4.52	dd	7.32, 1.95	6, 7	45.38			
6, 12	137.05				13, 17	39.82	1.8−1.9	m	
7, 11	35.00	2.1−2.2	m		14, 16	27.60	1.6−1.8	m	
8, 10	27.07	1.5−1.6	m		15	19. 88	1.6−1.8	m	
9	24.23	1.5−1.6	m		N−CH_3	39.82	2.32	s	
16, 17	95.37	5.11	dd						
N−CH_3	40.38	2.24	s						

[a] Solvent, benzene-d_6: s, singlet; d, doublet; dd, double-doublet; m, multiplet.

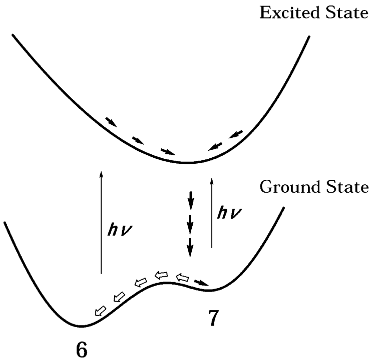

Figure 1. Isomerization processes between **6** and **7**.

the shorter wavelengths of visible spectrum. From the ^{1}H and ^{13}C NMR spectra, measured after light irradiation on **6**, the photoreaction product was assigned to 3,10-dimethyl-3,10-diazadispiro-[5.0.5.5]heptadeca-1,4,8,11-tetraene (**7**), a valence tautomer of **6** (Table 1). To our delight, **7** is exactly the desired dispiro compound characterized by a cycloheptane ring skeleton with vicinal spirocyclic dihydropyridine groups. The structural assignment of **7** was established by reference to the ^{1}H NMR spectra of **1**, **2**, and 1,2-bis(*N*-methyl-4-pyridyl)ethylene.[2,3,7] Although **7** was irradiated in MTHF at −196 °C with light of wavelength longer than 290 nm, no EPR spectrum due to the transition of a two-spin system was observed. This indicates that **7** is insensitive to light and, hence, is a highly stable species for a long peiod of time below room temperature. From this viewpoint, **7** differs markedly from related cyclomers obtained previously, where all of them undergo photochemical reactions by fission of a CC single bond to yield diradical intermediates at low temperatures.[6] On the other hand, **7** is thermolabile even under vacuum and, surprisingly, reverts back to **6** quantitatively by application of heat. The thermal isomerization will be accounted for in terms of a [3.3]-sigmatropic rearrangement. This is because the methylene chain is so long that the two six-membered rings are capable of facing each other to assume a sandwich-like form as the transition structure. Likewise, the sigmatropic rearrangement will be invoked to account for the photochemical isomerization from **6** to **7**. The processes of isomerization were followed both by the absorption spectroscopy and by the NMR spectral changes with elapse of time: The absorption spectrum of **7** changed into that of **6** on warming, and the resulting solution showed the spectrum of **7** upon irradiation. Under appropriate conditions, the conversions were almost reversible in a sealed tube. Figure 1 shows schematically most possible isomerization processes between **6** and **7**, where black arrows indicate the photochemical reaction and white ones, the thermal reaction.

In summary, **6** is a sensitive cyclomer to the ultraviolet and to the shorter wavelengths of visible spectrum, isomerizing into **7** by the rearrangement of a CC single bond at low temperatures. This behavior shows a marked distinction between **6** and related cyclomers,[6] the former undergoing no cleavage of a CC single bond to yield a diradical intermediate. In contrast, **7** is highly reactive to heat so that it is readily converted into **6** by the [3.3]-sigmatropic rearrangement at room temperature. Further details of **6** and **7** together with the MO theoretical results will be forthcoming elsewhere.

Supporting Information Available: Copies of UV−vis absorption and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The EPR spectrum observed at the early stage of reduction was extremely weak in intensity, and hence no absorption spectrum arising from the cation radical species could be identified. The EPR spectrum obtained by accumulation for 48 h was identified as $\mathbf{5}^{+}$ by means of a computer simulation, showing that the unpaired electron is confined to one of the pyridine rings.
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(10) (a) The reduction product exhibits a high reactivity to air oxygen as **1** and **2** do.[2,3,7] (b) Very weak signals in the ^{1}H NMR spectrum indicate the presence of a negligibly small amount of products other than the chief one, but no clear assignments were made for the products because of individual components not being isolated in our experimental arrangements.
(11) From our experimental results so far,[6] we assume that the two-electron reduction of $\mathbf{5}^{2+}$ favors the production of 2,2′-cyclomer with a meso form. However, it is also possible that the reduction leads to the production of 2,6′-cyclomer with a *dl* form. AM1 calculations reveal that the energy difference between the two is less than 1 kcal/mol.
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(13) Light irradiation was carried out with a Ushio 500-W high-pressure mercury lamp and Toshiba filters (UV-31 and L-42), which are transparent at wavelengths longer than 310 and 420 nm, respectively.

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