7,7-Dipyridyl-2,6-di-*tert*-butyl-*p*-quinone Methides: Synthesis, Complexation with Silver(I) Ion, and Oxidation to Their Pyridine *N*-Oxide

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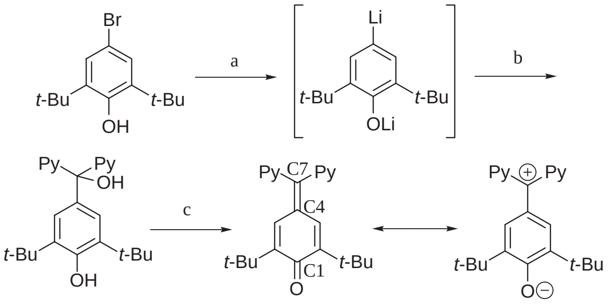
A series of 7,7-dipyridyl-*p*-quinone methides are prepared from the corresponding dipyridylketones with 4-lithio-2,6-di-*tert*-butylphenoxide followed by dehydration. 7,7-Bis(2-pyridyl)-*p*-quinone methide formed the binuclear Ag(I) complex in which the quinone methide rings are deformed to the boat form. Oxidation of 7,7-dipyridyl-*p*-quinone methides gave the corresponding bis(pyridine *N*-oxide)s.

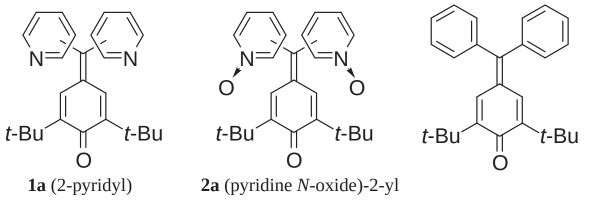
p-Quinone methides (*p*-QMs), a structural hybrid between *p*-benzoquinone and *p*-quinodimethane, are featured by their highly dipolar properties arising from the less symmetric structures and the tendency of aromatization of the central six-membered ring.[1] Highly dipolar π-electron systems have attracted considerable attention in relation to near-infrared dyes and nonlinear optics.[2] Although the parent *p*-QM is a highly reactive compound,[3] 7,7-diaryl *p*-QMs[4] are fairly stable, whose properties are well tunable by the substituents on the aryl groups. In this context, 7,7-dipyridyl *p*-QMs would be interesting molecules, because of the properties of pyridine such as basicity, oxidation to *N*-oxide, and complexation with the various transition metals.[5] Contrary to the numerous studies on 7,7-diphenyl *p*-QM derivatives, 7,7-dipyridyl *p*-QMs have not been studied. In order to explore the potential utility of the structural feature of *p*-QM for the novel functional dyes, we now report the synthesis and properties of a series of 7,7-dipyridyl *p*-QMs **1a**–**1c**, their bis(pyridine *N*-oxide)s **2a**–**2c**, and the structural feature of silver(I) complex of **1a** (Chart 1).

Scheme 1 shows the synthesis of dipyridyl *p*-QMs **1a**–**1c**. Reactions of 4-lithio-2,6-di-*tert*-butylphenoxide[6] with 0.25 equiv. of the corresponding dipyridyl ketones afforded diols **3a**–**3c** in moderate to good yields. Dehydration of **3a**–**3c** to **1a**–**1c** was accomplished by heating with $POCl_3$ in pyridine in good yields. *p*-QMs **1a**–**1c** are stable, orange crystalline substances.[7]



3a–**3c** **1a**–**1c** dipolar structure

Scheme 1. (a) *t*-BuLi (3.0 equiv.), ether, 0 °C, 1 h; (b) $Py_2C=O$ (0.25 equiv.), −78 °C, 1 h then rt, overnight (46% for **3a** (Py = 2-pyridyl), 32% for **3b** (Py = 3-pyridyl), 87% for **3c** (Py = 4-pyridyl)); (c) $POCl_3$ (5.0 equiv.), pyridine, reflux, overnight (62% for **1a**, 70% for **1b**, 82% for **1c**).



1a (2-pyridyl)
1b (3-pyridyl)
1c (4-pyridyl)

2a (pyridine *N*-oxide)-2-yl
2b (pyridine *N*-oxide)-3-yl
2c (pyridine *N*-oxide)-4-yl

4

Chart 1.

Table 1 summarizes the selected spectral data of **1a**–**1c** together with 7,7-diphenyl *p*-QM **4**.[8] *p*-QMs **1a**–**1c** showed the relatively low field shifts at C4 as well as high field shifts at C7 in their ^{13}C NMR chemical shifts. The C=O stretching frequency of **1a**–**1c** were observed at higher wavenumber than that of **4**, and the slightly low field shifts at C1 was also observed. These results indicate that **1a**–**1c** take smaller contribution of the dipolar structure than **4** due to the electron-withdrawing effect of the pyridyl groups. The cyclic voltammograms of **1a**–**1c** showed two reduction potentials, which were more positive than those of **4**. *p*-QMs **1a**–**1c** exhibit the absorption maxima at slightly shorter wavelength than **4**.

Figure 1 shows the ORTEP drawing of 2-pyridyl *p*-QM **1a**.[9] The bond lengths of C1–O1 and C4–C7 are 1.223 and 1.370(4) Å, respectively. *p*-QM **1a** takes a propeller conformation in which the *p*-QM moiety is almost planar while 2-pyridyl groups are twisted by the angle of 52.9 and 52.3°. In comparison with 7,7-diphenyl-2,6-dimethyl *p*-QM,[10] **1a** exhibits slightly shorter C=O bond length also suggesting the larger contribution of quinoid structure.

Although no change in absorption spectrum of **1a** was observed by the addition of silver(I) complexes, the prominent changes in ^1H NMR chemical shifts were observed.[11] This

Table 1. Selected spectral data of *p*-QMs **1a**–**1d**

Compounds	^{13}C NMR chemical shifts[a] δ/ppm			$\nu(C=O)$[b]/cm^{-1}	Reduction potentials[c]/V		λ_{max}[d]/nm (log ε)
	C1	C4	C7		E^1_{red}	E^2_{red}	
1a	186.31	132.55	149.41	1611	−1.43	−1.83	349 (4.45)
1b	186.01	132.02	146.57	1609	−1.40	−2.00[e]	360 (4.47)
1c	186.03	132.14	147.08	1610	−1.27	−1.63	346 (4.46)
4	185.84	129.54	155.63	1601	−1.55	−2.21[e]	365 (4.50)

[a]In $CDCl_3$. [b]KBr disk. [c]V vs Ag/Ag^+, in 0.1 M $n\text{-}Bu_4NClO_4$/DMF, sweep rate 100 mV s^{-1}, at 25 °C, $Fc/Fc^+ = +0.11$ V. [d]In cyclohexane. [e]Peak potential.

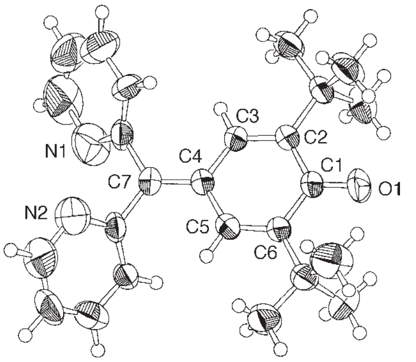


Figure 1. ORTEP drawing of **1a** (50% probability). Selected bond lengths (Å): C1–O1 1.223(4), C1–C2 1.481(4), C1–C6 1.480(4), C2–C3 1.338(4), C3–C4 1.453(4), C4–C5 1.457(4), C4–C7 1.370(4), C5–C6 1.344(4).

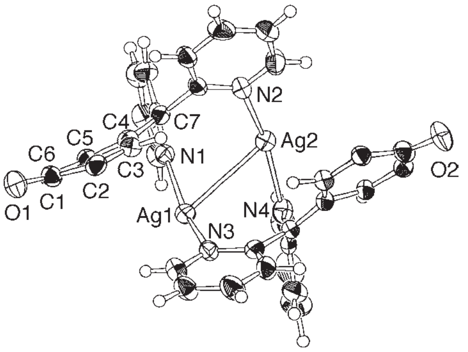


Figure 2. ORTEP drawing of silver(I) complex of **1a** along *c* axis (50% probability). *tert*-Butyl groups and BF_4^- ions are omitted for clarity. Selected bond lengths (Å) and angles (°): Ag1–Ag2 3.099(2), Ag1–N1 2.184(7), Ag1–N3 2.163(7), Ag2–N2 2.213(7), Ag2–N4 2.189(8), C1–O1 1.25(1), C1–C2 1.49(1), C2–C3 1.34(1), C3–C4 1.45(1), C4–C7 1.36(1), Ag2–Ag1–N1 67.3(2), Ag2–Ag1–N3 100.7(2), N1–Ag1–N3 157.4(2), Ag1–Ag2–N2 99.7(2), Ag1–Ag2–N4 65.2(2), N2–Ag2–N4 156.0(3).

changes of the chemical shifts were saturated by 1.0 equiv. of silver(I) ion, which suggested the formation of a 1:1 complex of **1a** and silver(I) ion. Single crystals of silver(I) complex of **1a** suitable for X-ray crystallographic analysis were obtained from a solution of **1a** in acetonitrile–ether involving an equivalent of $AgBF_4$.[12] The molecular structure (Figure 2) reveals that the complex adopts a binuclear coordination structure connected with two molecules of **1a**. Atomic distances of the Ag1–N1, Ag1–N3, Ag2–N2, and Ag2–N4 are in the range of 2.16–2.21 Å and Ag1–Ag2 is 3.10 Å. Although this short silver–silver contact is often observed in many binuclear silver(I) complexes, it is not thought to be indicative of any particular intermetallic interactions.[13] Compared with **1a**, it should be noted that the quinone methide rings are deformed to the boat form by the complexation.

The *N*-oxides **2a**–**2c** were prepared by oxidation of **1a**–**1c** with MCPBA in CH_2Cl_2 at 0 °C in good yields (84% for **2a**, 83% for **2b**, and 92% for **2c**) as stable yellow (**2a**) or orange (**2b** and **2c**) crystalline substances.[7] In the UV–vis measurement, 4-pyridyl derivative **2c** exhibits the most prominent effect, compared with the corresponding dipyridyl *p*-QM **1c**. Thus, the solution of **1c** in CH_2Cl_2 exhibits the longest absorption maxima at 348 nm which are red-shifted up to 412 nm by oxidation into **2c**. This bathochromic effect would be attributable to the effective conjugation between pyridine *N*-oxide groups and *p*-QM moiety; this absorption of **2c** in acetonitrile (λ_{max} 413 nm) disappeared by protonation at the oxygen atoms of pyridine *N*-oxide groups with one drop of 2 M H_2SO_4. On the other hand, although 2-pyridyl derivative **2a** also exhibits the absorption at around 400 nm, its intensity is quite weak. This weakness of the absorption intensity would be due to the steric congestion around C7 decreasing the coplanarity between the QM ring and pyridine *N*-oxide groups. On the contrary, the absorption of 3-pyridyl derivative **1b** (λ_{max} 365 nm) is blue-shifted by oxidation into **2b** (λ_{max} 346 nm).

In summary, we prepared the series of dipyridyl *p*-QMs **1a**–**1c**. 2-Pyridyl derivative **1a** forms the binuclear silver(I) complex in which the distortion of the QM ring is increased by the complexation. The difference of the properties dependent on the position of the nitrogen atoms appears by the oxidation into the corresponding *N*-oxides **2a**–**2c**. The preparation of metal complex of **1b** and **1c**, and other 7,7-bis(heteroaryl) *p*-QMs are now under investigation.

References and Notes

1 Reviews: a) A. B. Turner, *Quart. Rev.* **1964**, *18*, 347. b) H.-U. Wagner, R. Gompper, *The Chemistry of the Quinoid Compounds*, ed. by S. Patai, Wiley & Sons, London, **1974**, p. 1145. c) A. A. Volod'kin, V. V. Ershov, *Russ. Chem. Rev.* **1988**, *57*, 336. d) M. G. Peter, *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 555. e) P. Wan, B. Barker, L. Diao, M. Fischer, Y. Shi, C. Yang, *Can. J. Chem.* **1996**, *74*, 465.

2 a) R. Gompper, H.-U. Wagner, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1437. b) D. J. Williams, *Angew. Chem., Int. Ed. Engl.* **1988**, *23*, 690.

3 a) G. J. Leary, *Wood Sci. Technol.* **1980**, *14*, 21. b) S. M. Shevchenko, A. G. Apushkinskii, *Russ. Chem. Rev.* **1992**, *61*, 1. c) D. C. Thompson, J. A. Thompson, M. Sugumaran, P. Moldeus, *Chem.-Biol. Interact.* **1992**, *86*, 129.

4 For example: a) A. Bistrzycki, C. Herbst, *Chem. Ber.* **1903**, *36*, 2333. b) K. H. Meyer, *Justus Liebigs Ann. Chem.* **1920**, *420*, 134. c) R. Gompper, H.-U. Wagner, *Tetrahedron Lett.* **1968**, *9*, 165.

5 We recently synthesized the molecules having polypyridyl groups for supramolecular architectrure: a) K. Matsumoto, Y. Harada, T. Kawase, M. Oda, *Chem. Commun.* **2002**, 324. b) K. Matsumoto, M. Kannami, M. Oda, *Tetrahedron Lett.* **2003**, *44*, 2861. c) K. Matsumoto, M. Kannami, M. Oda, *Chem. Lett.* **2004**, *33*, 1096. See also: d) P. J. Steel, C. J. Sumby, *Chem. Commun.* **2002**, 322. e) P. J. Steel, C. J. Sumby, *Inorg. Chem. Commun.* **2002**, *5*, 323.

6 a) H. Kurata, T. Tanaka, M. Oda, *Chem. Lett.* **1999**, *28*, 749. b) H. Kurata, Y. Takehara, T. Kawase, M. Oda, *Chem. Lett.* **2003**, *32*, 538. c) H. Kurata, T. Shimoyama, K. Matsumoto, T. Kawase, M. Oda, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1327.

7 Spectroscopic data for the *p*-QMs **1a**–**1c** and their *N*-oxides **2a**–**2c** are described in the Supporting Information.

8 B. Koutek, M. Písová, M. Soucek, O. Exner, *Collect. Czech. Chem. Commun.* **1976**, *41*, 1676.

9 Crystal data for **1a**: $C_{25}H_{28}N_2O$, MW = 372.51, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.986(3)$, $b = 8.406(4)$, $c = 22.550(3)$ Å, $\beta = 96.61(1)°$, $V = 2256.9(10)$ Å^3, $Z = 4$, $D_{calcd} = 1.096$ g cm^{-3}, $T = 296$ K, Of the 5787 reflections which were collected, 5414 were unique ($R_{int} = 0.012$) used in refinement. $R1 = 0.063$ (2024 data $I > 2\sigma(I)$), $wR2 = 0.252$ (all data), GOF = 1.00, CCDC-289129.

10 T. W. Lewis, I. C. Paul, D. Y. Curtin, *Acta Crystallogr.* **1980**, *B36*, 70.

11 The change of the chemical shifts of **1a** by silver(I) ion are described in the Supporting Information.

12 Crystal data for the silver(I) complex of **1a**: $C_{50}H_{56}Ag_2B_2F_8N_4O_2$, MW = 1134.36, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.87(1)$, $b = 18.70(3)$, $c = 30.68(4)$ Å, $\beta = 95.82(4)°$, $V = 6205(51)$ Å^3, $Z = 4$, $D_{calcd} = 1.214$ g cm^{-3}, $T = 200$ K, Of the 58518 reflections which were collected, 13963 were unique ($R_{int} = 0.044$) used in refinement. $R1 = 0.073$ (5367 data, $I > 2\sigma(I)$), $wR2 = 0.248$ (all data), GOF = 0.99. CCDC-289130.

13 F. A. Cotton, X. Feng, M. Matusz, R. Poli, *J. Am. Chem. Soc.* **1988**, *110*, 7077.

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