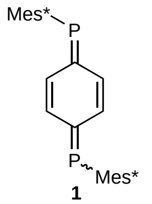
Synthesis, Structure, and Redox Properties of Diphosphathienoquinones**

Fumiki Murakami, Shigeru Sasaki, and
Masaaki Yoshifuji*

Although a variety of π-conjugated molecules containing low-coordinate phosphorus atoms is known,[1] only two stable phosphaquinoid compounds have been reported: diphosphaquinone **1** by Märkl et al.[2] and phosphaquinone **2** by us.[3] Diphosphathienoquinones **3** are expected to be more stable than **1** and still behave chemically and physically as a quinoid compound, since so-called heteroquinoid molecules which contain a heteroatom such as sulfur in place of one endocyclic C=C bond of quinoid compounds, generally have higher stability than their benzenoid counterparts without losing the inherent properties of the quinoid system.[4] Here we report a general synthetic route for diphosphaquinones and diphosphathienoquinones, and the synthesis, structure, and redox properties of the first diphosphathienoquinone **4**.



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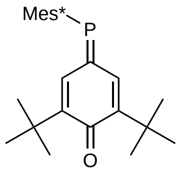

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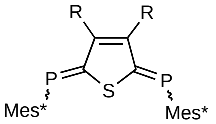
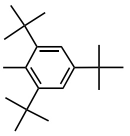
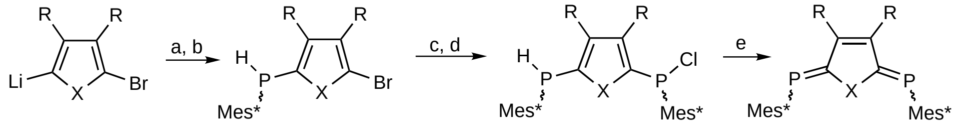


3: R = H
4: R = Br

Mes* =





5a: X = CH=CH, R = H
5b: X = S, R = H
5c: X = S, R = Br

6a: X = CH=CH, R = H (90%)
6b: X = S, R = H (76%)
6c: X = S, R = Br (57%)

7a: X = CH=CH, R = H (39%)
7b: X = S, R = H
7c: X = S, R = Br

1: X = CH=CH, R = H
3: X = S, R = H (86%)
4: X = S, R = Br (65% from **6c**)

Scheme 1. Synthesis of a diphosphaquinone and diphosphathienoquinones. a) Mes*PCl$_2$, Et$_2$O, −78 °C, b) LiAlH$_4$, Et$_2$O, 0 °C, c) *t*BuLi (**7a**, **7b**) or *n*BuLi (**7c**), Et$_2$O, −78 °C, d) Mes*PCl$_2$, Et$_2$O, −78 °C, e) KH, [18]crown-6, THF, room temperature.

Diphosphaquinone **1** was prepared by dechlorination of 1,4-bis(chlorophosphanyl)benzene with zinc, but the product was contaminated with secondary phosphanes because of over-reduction.[2] To synthesize diphosphaquinones selectively, we employed 1,6-dehydrochlorination of (chlorophosphanyl)phosphanylbenzene or -thiophene precursors **7** as the final step (Scheme 1). Compounds **7** were prepared by stepwise introduction of phosphanyl and chlorophosphanyl groups on the aromatic ring by reaction of the corresponding aryllithium with Mes*PCl$_2$[5] (Mes* = 2,4,6-tri-*tert*-butylphenyl) and obtained as mixtures of diastereomers. Deprotonation of **7a** and **7b** with an excess of potassium hydride in the presence of [18]crown-6 afforded diphosphaquinone **1** and diphosphathienoquinone **3** as inseparable 1:1 mixtures of (*E*)-**1** ($\delta_P = 261$ ppm) and (*Z*)-**1** ($\delta_P = 263$ ppm) and of (*E*,*Z*)-**3** ($\delta_P = 209$ ppm (d, $J(P,P) = 264$ Hz), 192 ppm (d, $J(P,P) = 264$ Hz)) and (*Z*,*Z*)-**3** ($\delta_P = 197$) isomers. To enhance the preference for the *Z*,*Z* isomer by steric repulsion between the bulky Mes* and other substituents, bromine atoms were introduced into the 3- and 4-positions of the thiophene ring, and **7c** was dehydrochlorinated to afford air-stable orange prisms of **4** as a single *Z*,*Z* isomer.

The ^{1}H NMR spectrum (500 MHz, CD$_2$Cl$_2$) of **4** reflected its highly symmetrical structure, and only three signals corresponding to aromatic, *o*-*t*Bu, and *p*-*t*Bu protons were observed. The ^{13}C NMR spectrum (126 MHz, CD$_2$Cl$_2$) was also indicative of a symmetrical structure, and three signals corresponding to the C atoms close to the phosphorus atoms were observed as a pseudotriplet, typical of an AXX′ pattern.[6] The ^{31}P NMR chemical shifts of diphosphathienoquinones (*E*,*Z*)-**3**, (*Z*,*Z*)-**3**, and **4** were observed upfield relative to those of diphosphaquinones **1** and phosphaquinone **2**. The molecular structure of **4** was further studied by X-ray crystallography (Figure 1) and compared with that of thienylphosphane **6c**. The two exocyclic P=C bonds adopt a *Z* configuration with bond lengths of 1.712(2) and 1.714(2) Å, which are longer than those of typical sterically protected phosphaalkenes (ca. 1.68 Å)[7] but comparable to that of phosphaquinone **2** (1.705(2) Å). The structural change of the five-membered ring from an "aromatic" thiophene to a thienoquinoid structure was revealed by comparing **4** with **6c**. The single bonds C1−C2, C3−C4, C4−S1, and S1−C1 were longer than the corresponding values of **6c** by 0.049, 0.060, 0.031, and 0.024 Å, respectively, while the double bond C2−C3 was shorter by 0.063 Å. The five-membered ring and two exocyclic phosphorus atoms are planar with a maximum

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[*] Prof. Dr. M. Yoshifuji, Dr. F. Murakami, Dr. S. Sasaki
Department of Chemistry
Graduate School of Science
Tohoku University
Aoba, Sendai 980-8578 (Japan)
Fax:(+81)22-217-6562
E-mail: yoshifj@mail.cc.tohoku.ac.jp

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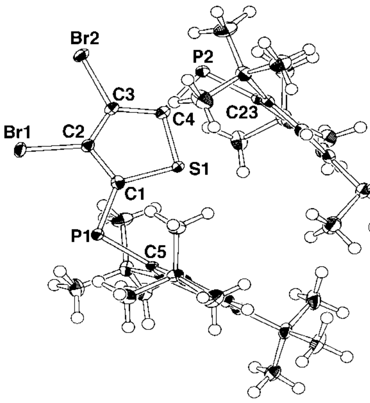

Figure 1. ORTEP plot of **4** with 50% probability thermal ellipsoids. Selected bond lengths [Å] and angles [°]: P1-C1 1.712(2), P2-C4 1.714(2), C1-C2 1.416(3), C2-C3 1.359(3), C3-C4 1.415(3), C4-S1 1.743(2), C1-S1 1.751(2); C5-P1-C1 98.1(1), C23-P2-C4 100.6(1), P1-C1-C2 126.0(2), P1-C1-S1 126.0(1), C2-C1-S1 108.0(2), C1-C2-C3 115.2(2), C2-C3-C4 114.3(2), C3-C4-S1 108.8(2), P2-C4-C3 124.7(2), P2-C4-S1 126.4(1), C4-S1-C1 93.6(1), S1-C1-C2 108.0(2).

deviation from the least-squares plane of 0.0209 Å (C3). However, two *p*-*t*Bu groups are located very close to each other, and the whole diphosphathienoquinoid skeleton is twisted as a result of steric repulsion between them (C5-P1-P2-C23 torsion angle 29.7°).

In analogy with most other quinoid molecules, **4** was expected to be reduced stepwise to the dianion via a radical anion (semiquinone). This was confirmed by cyclic voltammetry of **4** (Figure 2), in which the first reversible ($^1E_{1/2} = -1.50$ V versus Ag/Ag$^+$) and the second irreversible ($^2E_\mathrm{P} = -2.49$ V) redox waves were observed. The first reduction potential, which was significantly lower than those of typical phosphaalkenes (ca. -2.2 V),[8] and the second are very close to that of phosphaquinone **2** ($^1E_{1/2} = -1.55$ V, $^2E_\mathrm{P} = -2.45$), but the radical anion of **4** has enhanced stability. The EPR spectrum of $\mathbf{4}^{\bullet-}$ obtained by reduction of **4** with sodium metal (Figure 3a) in THF at 293 K consisted of four lines resulting from hyperfine coupling (hfc) with two nonequivalent ^{31}P nuclei (a(P1) = 9.3, a(P2) = 2.1 mT, $g = 2.007$). The EPR spectrum of the frozen solution at 77 K (Figure 3b) was interpreted by assuming axial symmetric hfc and g tensors with a dominant contribution from $a_{\parallel}$(P1) (27.7 mT) and other minor contributions.[9] As observed for phosphaquinone **2**, the isotropic and anisotropic hfc constants were much larger than those of radical anions of typical phosphaalkenes but very close to those of phosphanyl radicals[10] which suggests significant localization of an unpaired electron on the 3p orbital of one phosphorus atom (P1; 69% by comparison with atomic hfc constants[11]) and considerable contribution of thiophene-bearing localized phosphorus radical and anion centers. Further synthetic studies on phosphathienoquinoid and phosphaquinoid molecules are in progress.

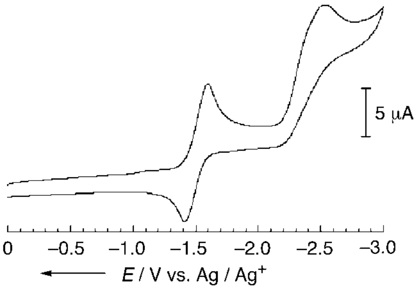

Figure 2. Cyclic voltammogram of **4** at 293 K. Conditions: 10^{-4} M in THF with 0.1 M $n\mathrm{Bu_4NClO_4}$ as a supporting electrolyte; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01 M $\mathrm{AgNO_3}$ in acetonitrile with 0.1 M $n\mathrm{Bu_4NClO_4}$ ($E_{1/2}$(ferrocene/ferricinium) = 0.180 V); scan rate: 50 mV s^{-1}.

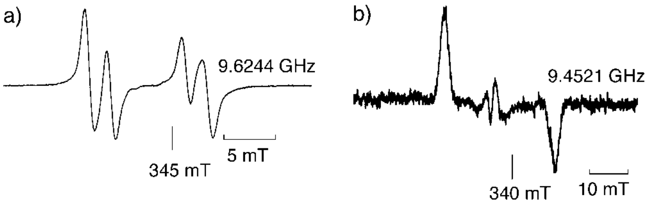

Figure 3. EPR spectra obtained at 295 K (a) and 77 K (b) after reduction of **4** with sodium metal in THF.

Experimental Section

7c: A solution of *tert*-butyllithium (2.1 mL, 1.50 M in *n*-pentane) was added to a solution of **6c** (669 mg, 1.12 mmol) in diethyl ether (15 mL) at 0 °C. The solution was stirred for 20 min at 0 °C and added to a solution of Mes*$\mathrm{PCl_2}$ (417 mg, 1.20 mmol) in diethyl ether (15 mL) at −78 °C. After stirring for 30 min at −78 °C and 10 h at 20 °C, the mixture was washed with saturated NaCl solution, dried over anhydrous $\mathrm{MgSO_4}$, and concentrated to afford crude **7c** almost quantitatively. **7c**: colorless crystals; ^{31}P NMR (81 MHz, $\mathrm{CDCl_3}$): $\delta = 68.8$ (s), -67.4 (d, J(P,H) = 229 Hz), 68.1 (s), -65.8 ppm (d, J(P,H) = 230 Hz).

4: A solution of **7c** in THF (10 mL) was added to a suspension of KH (192 mg, 40 wt% dispersion in mineral oil) and [18]crown-6 (766 mg, 2.90 mmol) in THF (10 mL) at 20 °C, and the mixture was refluxed for 30 min. Excess KH was decomposed with water (ca. 10 mL) at room temperature, and the mixture was washed with saturated NaCl solution, dried over anhydrous $\mathrm{MgSO_4}$, and purified by column chromatography ($\mathrm{Al_2O_3}$/benzene) and recrystallization from benzene to give **4** (578 mg, 0.729 mmol, 65%). **4**: orange plates (benzene), m.p. 173.0–175.0 °C (decomp); ^{1}H NMR (500 MHz, $\mathrm{CD_2Cl_2}$): $\delta = 7.25$ (4H, br s, arom.-*m*), 1.32 (36H, s, C(CH_3)$_3$-*o*) 1.20 ppm (18H, s, C(CH_3)$_3$-*p*); ^{13}C{^{1}H} NMR (126 MHz, $\mathrm{CD_2Cl_2}$): $\delta = 172.37$ (AXX′, ^1J(P,C) + ^3J(P′,C) = 73.6 Hz, P=*C*), 154.76 (s, Mes*-*o*), 151.37 (s, Mes*-*p*), 134.90 (AXX′, ^1J(P,C) + ^5J(P′,C) = 54.2 Hz, Mes*-*ipso*), 128.74 (AXX′, ^2J(P,C) + ^3J(P′,C) = 43.3 Hz, quinone-3), 122.61 (s, Mes*-*m*), 38.46 (s, *C*(CH$_3$)$_3$-*o*), 35.28 (s, *C*(CH$_3$)$_3$-*p*), 33.05 (AXX′, ^4J(P,C) + ^8J(P′,C) = 6.8 Hz, C(*C*H$_3$)$_3$-*o*), 31.49 ppm (s, C(*C*H$_3$)$_3$-*p*); ^{31}P NMR (81 MHz, $\mathrm{CD_2Cl_2}$): $\delta = 211.2$ ppm (s); UV/Vis (hexanes): λ_max (lgε) = 466 (4.39), 370 (3.72), 274 nm (3.91); FABMS *m*/*z* (%): 794 (56) [M^++4], 792 (91) [M^++2], 790 (45) [M^+], 713 (8) [M^++2 − Br], 711 (5) [M^+ − Br], 57 (62) [*t*Bu$^+$]; HRMS (70 eV, EI): found: *m*/*z* 790.2114; calcd for $\mathrm{C_{40}H_{58}P_2SBr_2}$: 790.2101.

Crystal data of **4**: $\mathrm{C_{40}H_{58}P_2SBr_2}$, $M_\mathrm{r} = 792.71$, red prisms from benzene, crystal dimensions 0.25 × 0.25 × 0.20 mm^3. $T = 115$ K, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.531(2)$, $b = 18.982(4)$, $c = 10.273(5)$ Å, $\alpha = 95.462(9)$, $\beta = 115.92(3)$, $\gamma = 82.28(2)°$, $V = 2002(1)$ Å^3, $Z = 2$, $\rho_\mathrm{calcd} = 1.315$ g cm^{-3}, $\mu = 2.188$ mm^{-1}, $F(000) = 828.00$, 6920 reflections measured ($2\theta_\mathrm{max} = 51.1°$), $R_\mathrm{int} = 0.030$; 6920 observed reflections [$I > 0.00\sigma(I)$], 639 variable parameters. $R = 0.037$, $R_\mathrm{w} = 0.043$, GOF $S = 1.27$ for observed reflections [$I > 0.00\sigma(I)$] and $R1 = 0.030$ for [$I > 2.00\sigma(I)$]. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.43 e Å^{-3}. CCDC-180101 (**4**) and -180102 (**6c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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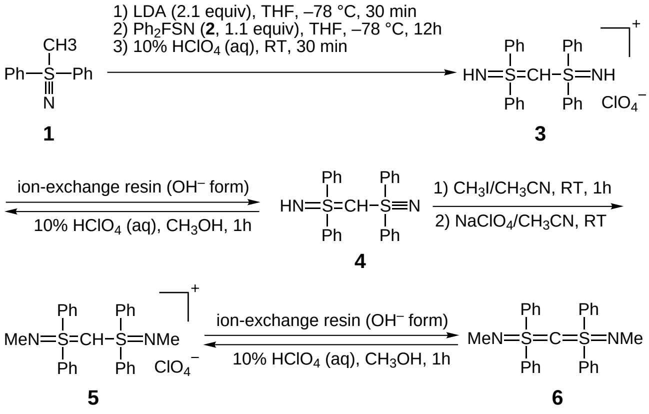
Synthesis and Structure of (MeN)Ph$_2$S=C=SPh$_2$(NMe)

Takayoshi Fujii, Tomio Ikeda, Toshie Mikami, Tetsuya Suzuki, and Toshiaki Yoshimura*

(X)R$_2$S=C=SR$_2$(X) can be regarded as the isoelectronic carbon analogue of the [(X)R$_2$S=N=SR$_2$(X)]$^+$ ion (R = Ar, alkyl; X = lone pair, NH, O).[1] There has, however, been little reported on this compound to date.[2] In view of its chemical properties and structural features, investigation of this compound has posed an interesting challenge. Herein, we report the first synthesis, isolation, and crystal structure of (MeN)Ph$_2$S=C=SPh$_2$(NMe) (**6**), prepared by the α-proton abstraction of a new type of iminosulfonium ylide [(MeN)Ph$_2$S=CH−SPh$_2$(NMe)]$^+$ (Scheme 1).



Scheme 1. Synthesis of **6**.

α-Lithiation of methyldiphenyl-λ^6-sulfanenitrile (**1**)[3a] with lithium diisopropylamide (LDA), followed by treatment with fluorodiphenyl-λ^6-sulfanenitrile (**2**)[3b] and acidification with perchloric acid afforded **3** in 66% yield. This compound was further treated with ion-exchange resin IRA-410 (OH$^-$ form) to give **4**[4–6] almost quantitatively. The reaction of **4** with methyl iodide in CH$_3$CN at room temperature and then treatment with NaClO$_4$ afforded precursor **5**, which was isolated in 26% yield by recrystallization from MeOH and diethyl ether.[7] The desired compound **6** was prepared in essentially quantitative yield by passing a methanolic solution of **5** through a column of the above basic resin.[6] The compositions of **3**–**6** were identified by NMR (except for **4**) and IR spectroscopy, as well as elemental analysis, and the molecular structures of **5** and **6** were determined by X-ray crystallographic analysis (Figure 1 and 2).[8]

The X-ray structure of **6** indicates the following characteristic properties (Figure 2). Each sulfur center is associated with one imido and two phenyl groups, in a pseudotetrahedral arrangement. The bond angles N1-S1-C1 and

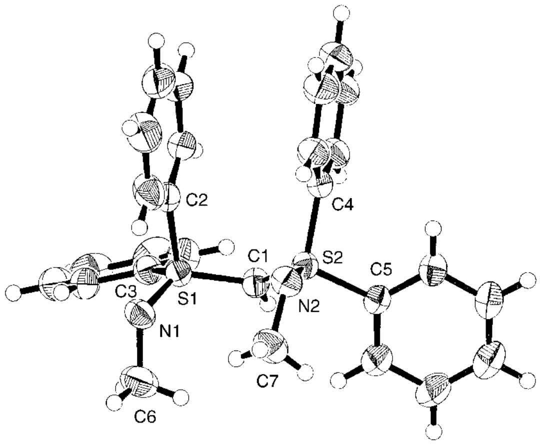


Figure 1. ORTEP drawing of **5** (50% probability thermal ellipsoids for all non-hydrogen atoms, perchlorate anion is omitted for clarity). Selected bond lengths [Å] and angles [°]: S1-N1 1.526(2), S1-C1 1.695(2), S1-C2 1.780(3), S1-C3 1.802(3), S2-N2 1.531(2), S2-C1 1.691(2), S2-C4 1.788(3), S2-C5 1.802(3), N1-C6 1.479(4), N2-C7 1.469(4); N1-S1-C1 123.1(1), N1-S1-C2 103.4(1), N1-S1-C3 112.5(1), C1-S1-C2 107.8(1), C1-S1-C3 102.4(1), C2-S1-C3 106.6(1), N2-S2-C1 119.6(1), N2-S2-C4 103.4(1), N2-S2-C5 115.4(1), C1-S2-C4 110.7(1), C1-S2-C5 102.1(1), C4-S2-C5 104.9(1), S1-N1-C6 117.3(2), S2-N2-C7 118.0(2), S1-C1-S2 118.0(1).

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[*] Prof. Dr. T. Yoshimura, Dr. T. Fujii, T. Ikeda, T. Mikami, T. Suzuki
Department of Material Systems Engineering
and Life Science
Faculty of Engineering
Toyama University
Gofuku, Toyama 930-8555 (Japan)
Fax: (+81) 76-445-6850
E-mail: yosimura@eng.toyama-u.ac.jp