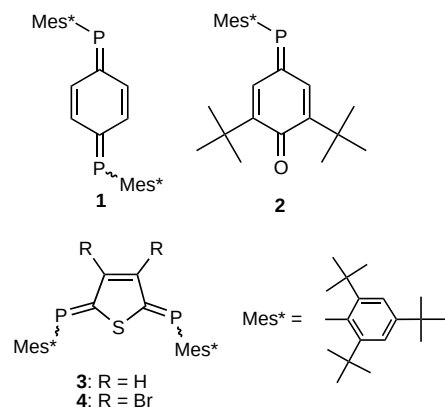


Synthesis, Structure, and Redox Properties of Diphosphathienoquinones**

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 phosphaquinoide compounds have been reported: diphosphaquinone **1** by Märkl et al.^[2] and phosphaquinoone **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**.

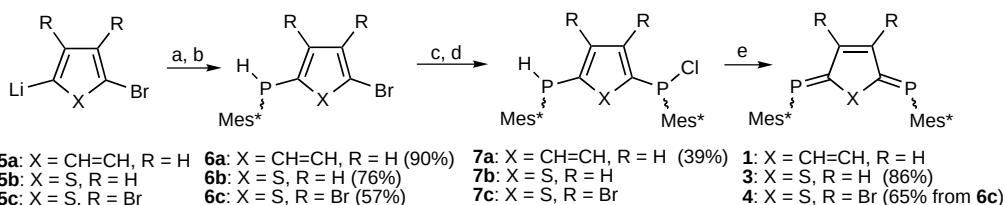


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[**] Financial support by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (Nos. 12740335, 08454193, and 09239101) is gratefully acknowledged. F.M. thanks the Japan Society for the Promotion of Science for a JSPS Postdoctoral Fellowship. The authors also thank the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University, for the measurement of 500 MHz NMR and mass spectra. This work was partially carried out in Advanced Instrumental Laboratory for Graduate Research of Department of Chemistry, Graduate School of Science, Tohoku University.

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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



Scheme 1. Synthesis of a diphosphaquinone and diphosphathienoquinones. a) Mes*PCl₂, Et₂O, -78 °C, b) LiAlH₄, Et₂O, 0 °C, c) *t*BuLi (**7a**, **7b**) or *n*BuLi (**7c**), Et₂O, -78 °C, d) Mes*PCl₂, Et₂O, -78 °C, e) KH, [18]crown-6, THF, room temperature.

with Mes*PCl₂^[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** (δ_p = 261 ppm) and (*Z*)-**1** (δ_p = 263 ppm) and of (*E,Z*)-**3** (δ_p = 209 ppm (d, $J(\text{P,P})$ = 264 Hz), 192 ppm (d, $J(\text{P,P})$ = 264 Hz)) and (*Z,Z*)-**3** (δ_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 ¹H NMR spectrum (500 MHz, CD₂Cl₂) 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 ¹³C NMR spectrum (126 MHz, CD₂Cl₂) 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 ³¹P NMR chemical shifts of diphosphathienoquinones (*E,Z*)-**3**, (*Z,Z*)-**3**, and **4** were observed upfield relative to those of diphosphaquinones **1** and phosphaquinoone **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 phosphalkenes (ca. 1.68 Å)^[7] but comparable to that of phosphaquinoone **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

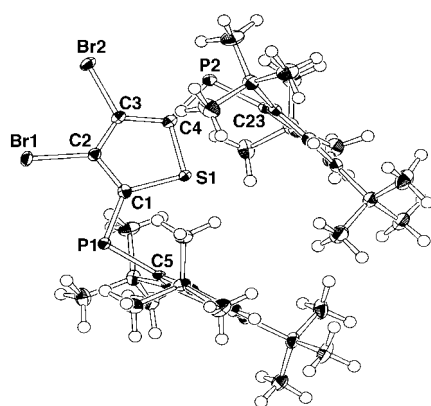


Figure 1. ORTEP plot of **4** with 50% probability thermal ellipsoids. Selected bond lengths [Å] and angles [°]: P1–C1 1.712(2), P2–C4 1.714(2), C1–C2 1.416(3), C2–C3 1.359(3), C3–C4 1.415(3), C4–S1 1.743(2), C1–S1 1.751(2), C5–P1–C1 98.1(1), C23–P2–C4 100.6(1), P1–C1–C2 126.0(2), P1–C1–S1 126.0(1), 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 ($E_{1/2} = -1.50$ V versus Ag/Ag⁺) and the second irreversible ($E_p = -2.49$ V) redox waves were observed. The first reduction

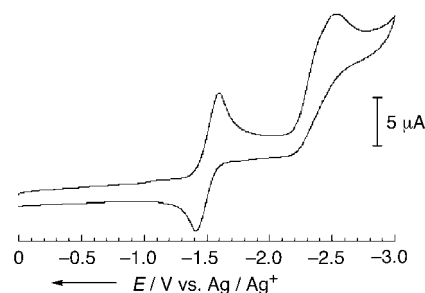


Figure 2. Cyclic voltammogram of **4** at 293 K. Conditions: 10^{-4} M in THF with 0.1 M $n\text{Bu}_4\text{NClO}_4$ as a supporting electrolyte; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01 M AgNO₃ in acetonitrile with 0.1 M $n\text{Bu}_4\text{NClO}_4$ ($E_{1/2}$ (ferrocene/ferricinium) = 0.180 V); scan rate: 50 mV s⁻¹.

potential, which was significantly lower than those of typical phosphalkenes (ca. -2.2 V),^[8] and the second are very close to that of phosphquinone **2** ($E_{1/2} = -1.55$ V, $E_p = -2.45$), but the radical anion of **4** has enhanced stability. The EPR spectrum of **4**^{•−} 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 ³¹P nuclei ($a(\text{P1}) = 9.3$, $a(\text{P2}) = 2.1$ 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 $a_{\parallel}(\text{P1})$ (27.7 mT) and other

minor contributions.^[9] As observed for phosphquinone **2**, the isotropic and anisotropic hfc constants were much larger than those of radical anions of typical phosphalkenes 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 phosphquinoid molecules are in progress.

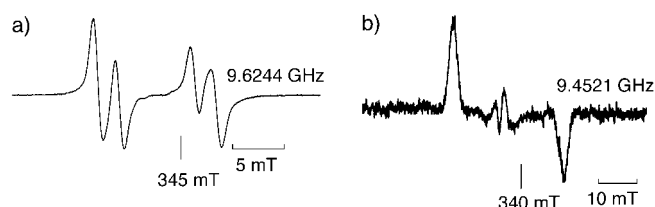


Figure 3. EPR spectra obtained at 295 K (a) and 77 K (b) after reduction of **4** with sodium metal in THF.

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*PCl₂ (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 MgSO₄, and concentrated to afford crude **7c** almost quantitatively. **7c**: colorless crystals; ³¹P NMR (81 MHz, CDCl₃): $\delta = 68.8$ (s), -67.4 (d, $J(\text{P,H}) = 229$ Hz), 68.1 (s), -65.8 ppm (d, $J(\text{P,H}) = 230$ 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 MgSO₄, and purified by column chromatography (Al₂O₃/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); ¹H NMR (500 MHz, CD₂Cl₂): $\delta = 7.25$ (4H, brs, arom.-*m*), 1.32 (36H, s, C(CH₃)₃-*o*) 1.20 ppm (18H, s, C(CH₃)₃-*p*); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): $\delta = 172.37$ (AXX', $^1J(\text{P,C}) + ^3J(\text{P',C}) = 73.6$ Hz, P=C), 154.76 (s, Mes*-*o*), 151.37 (s, Mes*-*p*), 134.90 (AXX', $^1J(\text{P,C}) + ^3J(\text{P',C}) = 54.2$ Hz, Mes*-*ipso*), 128.74 (AXX', $^2J(\text{P,C}) + ^2J(\text{P',C}) = 43.3$ Hz, quinone-3), 122.61 (s, Mes*-*m*), 38.46 (s, C(CH₃)₃-*o*), 35.28 (s, C(CH₃)₃-*p*), 33.05 (AXX', $^4J(\text{P,C}) + ^4J(\text{P',C}) = 6.8$ Hz, C(CH₃)₃-*o*), 31.49 ppm (s, C(CH₃)₃-*p*); ³¹P NMR (81 MHz, CD₂Cl₂): $\delta = 211.2$ 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) [$M^+ + 2 - \text{Br}$], 711 (5) [$M^+ - \text{Br}$], 57 (62) [*t*Bu⁺]; HRMS (70 eV, EI): found: m/z 790.2114; calcd for C₄₀H₅₈P₂SBr₂: 790.2101.

Crystal data of **4**: C₄₀H₅₈P₂SBr₂, $M_r = 792.71$, red prisms from benzene, crystal dimensions 0.25 × 0.25 × 0.20 mm³. $T = 115$ K, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.531(2)$, $b = 18.982(4)$, $c = 10.273(5)$ Å, $\alpha = 95.462(9)$, $\beta = 115.92(3)$, $\gamma = 82.28(2)^\circ$, $V = 2002(1)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 1.315$ g cm⁻³, $\mu = 2.188$ mm⁻¹, $F(000) = 828.00$, 6920 reflections measured ($2\theta_{\text{max}} = 51.1^\circ$), $R_{\text{int}} = 0.030$; 6920 observed reflections [$I > 0.00\sigma(I)$], 639 variable parameters. $R = 0.037$, $R_w = 0.043$, 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

Received: March 5, 2002 [Z18830]

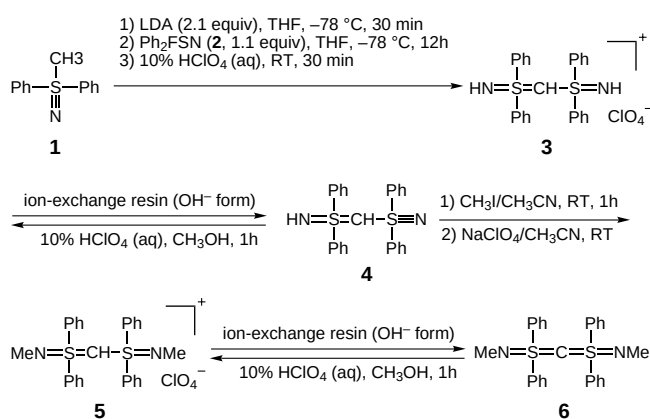
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Synthesis and Structure of (MeN)Ph₂S=C=SPh₂(NMe)

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(X)R₂S=C=SR₂(X) can be regarded as the isoelectronic carbon analogue of the [(X)R₂S=N=SR₂(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)Ph₂S=C=SPh₂(NMe) (**6**), prepared by the α -proton abstraction of a new type of iminosulfonium ylide [(MeN)Ph₂S=CH-SPh₂(NMe)]⁺ (Scheme 1).

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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 CH₃CN at room temperature and then treatment with NaClO₄ 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 pseudo-tetrahedral arrangement. The bond angles N1-S1-C1 and

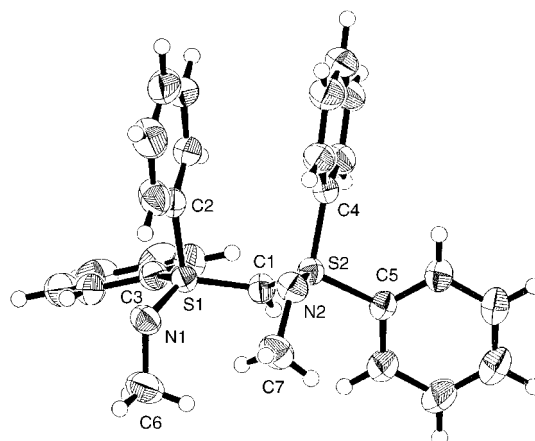


Figure 1. ORTEP drawing of **5** (50 % probability thermal ellipsoids for all non-hydrogen atoms, perchlorate anion is omitted for clarity). Selected bond lengths [Å] and angles [°]: S1-N1 1.526(2), S1-C1 1.695(2), S1-C2 1.780(3), S1-C3 1.802(3), S2-N2 1.531(2), S2-C1 1.691(2), S2-C4 1.788(3), S2-C5 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).