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CRYSTAL STRUCTURE AND COMPLEXATION BEHAVIOR OF QUINONEDIIMINE BEARING THIADIAZOLE UNIT

Mendra T. S. Ritonga, Harumi Shibatani, Hidehiro Sakurai, Toshiyuki Moriuchi, and Toshikazu Hirao*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan
E-mail: hirao@chem.eng.osaka-u.ac.jp

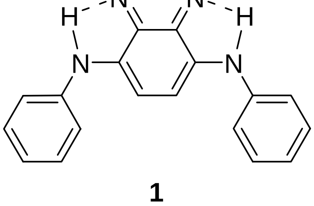
Abstract – The single crystal X-Ray structure determination of aniline oligomers composed of a benzothiadiazole unit revealed the twisted conformation in the crystal state. Despite π-conjugation, the quinonediimine (**2**) exhibited the more twisted conformation compared with the *p*-phenylenediamine (**1**). The benzothiadiazole ring was also found to control the arrangement through π-π interaction in the crystal packing. The controlled complexation of **2** with $Pd(MeCN)_4(BF_4)_2$ was achieved by the *N*-heterocyclic coordination sites.

INTRODUCTION

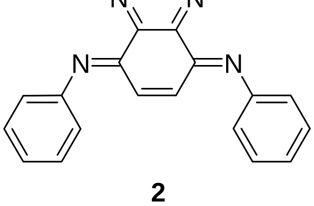
π-Conjugated polymers and oligomers have attracted much attention in the application to electrical materials depending on their electrical properties.[1-7] Their function is expected to be modified dramatically by a dopant or acceptor (or donor) unit. Controlling a band gap may afford a polymer with the desired electrical and optical properties, and reduction of the band gap to approximately zero is expected to afford a conducting polymer.[8,9] One of the most successful approaches to the low band-gap polymers depends on an alternating sequence of donor-acceptor units in the π-conjugated polymer chain.[10-22] Polyanilines are one of the promising electrically conducting π-conjugated polymers with chemical stability. Introduction of a benzothiadiazole (BT) unit into a backbone of aniline polymers or oligomers has been demonstrated to lower a HOMO-LUMO gap,[23,24] which is considered to be affected by the π-conjugation. Furthermore, a π-π interaction between the BT aromatic rings may be possible in a crystal packing. This interaction could induce architecturally controlled self-assembly, leading to molecular aggregates in a solid state. Two nitrogen atoms of the quinonediimine (qd) moiety in the emeraldine base of polyanilines have been revealed to be capable of complexation, giving novel conjugated complexes under coordination control.[25-30] The controlled complexation with the redox-active π-conjugated ligand, *N*,*N'*-bis(4'-dimethylaminophenyl)-1,4-benzoquinonediimine, has been achieved to afford the conjugated polymeric complex, the conjugated trimetallic macrocycle, or the conjugated bimetallic complex depending on the coordination mode.[31,32] The BT unit is expected to provide a conjugated bidentate coordination site. From these points of view, we herein report the crystal structure of aniline oligomers composed of a BT unit and the controlled complexation with $Pd(MeCN)_4(BF_4)_2$.

RESULTS AND DISCUSSION

The *p*-phenylenediamine (**1**) composed of a BT unit was prepared by the reaction of 4,7-dibromo-2,1,3-benzothiadiazole with aniline.[23] X-Ray crystallographic analysis was performed in order to elucidate the π-conjugated structure of **1** (Figure 1a and Table 1). The selected bond distances and angles are listed in Table 2. The dihedral angles of N(1)-C(2)-C(1)-N(2) and N(11)-C(102)-C(101)-N(12) are -0.9° and -0.4°, respectively. H(1) and H(2) are faced on the BT nitrogens. The distances of N(2)-H(1) and N(12)-H(2) are 2.53 and 2.54 Å, respectively. The angles of N(1)-C(2)-C(1) and N(11)-C(102)-C(101) are 117.0° and 117.5°, respectively, smaller than those of N(1)-C(2)-C(3) and N(11)-C(102)-C(103) (127.1° and 126.5°). These data indicate that intramolecular hydrogen bonds exist between the imine nitrogens of the BT ring and the amines adjacent to the heterocycle. The benzene rings in a *syn*-conformation are twisted against each other. The steric interactions between the hydrogen atom at C(3) and the hydrogen atom at C(9) (H(3)-H(8), 2.34 Å), and the hydrogen atom at C(103) and the hydrogen atom at C(109) (H(9)-H(14), 2.29 Å) result in a conformation with a dihedral angle of 46.0° and 44.2°, respectively, between the BT ring and each adjacent benzene ring. Furthermore, the BT moieties of **1** are oriented in a face-to-face manner to form π-stacks in the crystal packing, with an interplanar distance of ca. 3.5 Å between the neighboring BT moieties (Figure 2). The formation of π-stacks in the crystal packing is also considered to affect the twisted conformation of the benzene rings.

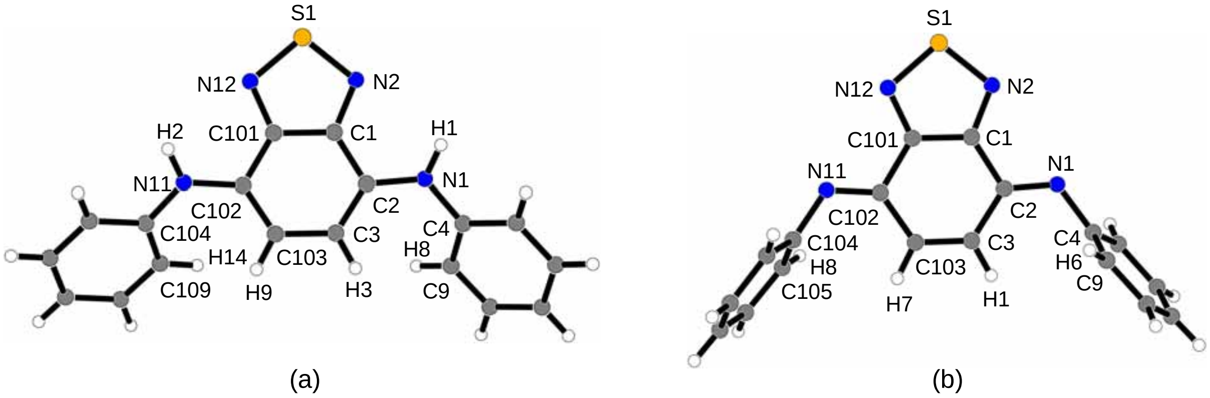


1



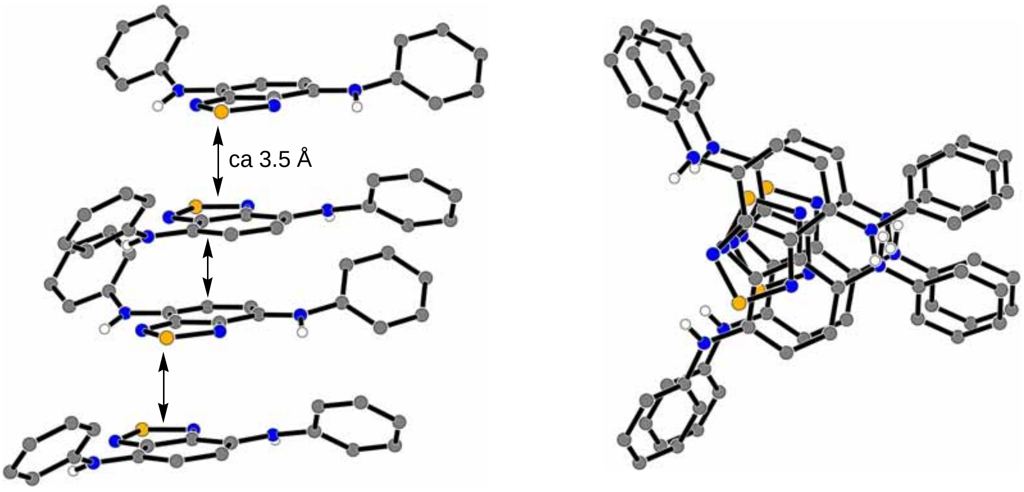
2

The *p*-phenylenediamine (**1**) was chemically oxidized to the *syn*-quinonediimine (**2**) by treatment with 1.2 molar amounts of Ag_2O.[23] The single crystal X-Ray structure determination of **2** revealed the twisted conformation as observed in the crystal structure of **1** (Figure 1b). Due to π-conjugation of **2**, the orientation of each benzene ring in a *syn*-conformation should be within a limited range of location planar to the BT moiety. The steric interactions between the hydrogen atom at C(3) and the hydrogen atom at C(9) (H(1)-H(6), 2.96 Å), and the hydrogen atom at C(103) and the hydrogen atom at C(105) (H(7)-H(8), 3.03 Å), however, cause the benzene ring of **2** to rotate away from this orientation, resulting in a conformation with a dihedral angle of 74.6° and 77.7°, respectively, between the BT ring and each adjacent benzene ring. The formation of the quinonediimine moiety by the oxidation of the phenylenediamine moiety reduced the C-N distances (**1**: C(2)-N(1), 1.388 Å; C(102)-N(11), 1.395 Å; **2**: C(2)-N(1), 1.283 Å; C(102)-N(11), 1.284 Å), which are considered to induce these large dihedral angles compared with those of **1**. Furthermore, the BT moieties of **2** are arranged in a face-to-face manner with an interplanar distance of ca. 3.5 Å through π-π interaction, together with extended π-stacking in the crystal packing (Figure 3). This extended π-stacking in the crystal packing is also considered to induce the twisted conformation of the benzene rings.



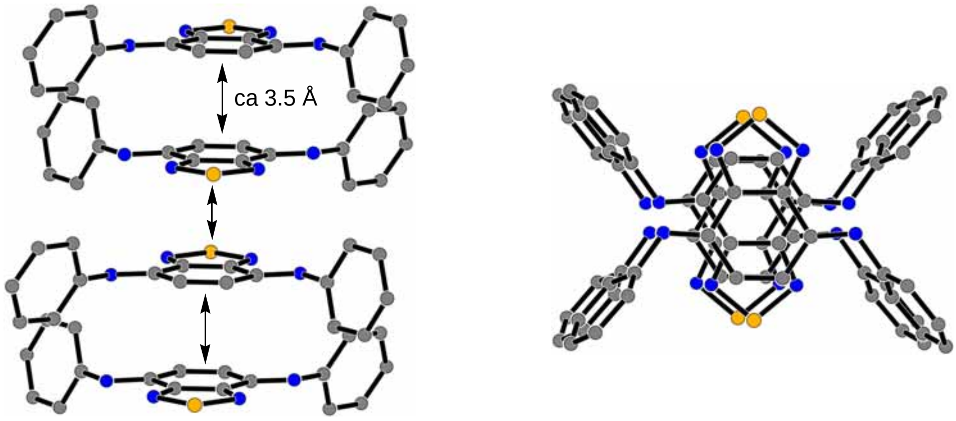
(a) (b)

Figure 1. Molecular structures of (a) **1** and (b) **2**.



(a) (b)

Figure 2. (a) Side view and (b) top view of the crystal packing diagram of **1** showing extended π-stacking.



(a) (b)

Figure 3. (a) Side view and (b) top view of the crystal packing diagram of **2** showing extended π-stacking.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{18}H_{14}N_4S$	$C_{18}H_{12}N_4S$
fw	318.40	316.38
cryst syst	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	6.9508(1)	6.8130(4)
b, Å	29.3796(7)	25.060(2)
c, Å	15.1153(3)	8.9970(7)
β, deg		94.018(3)
V, Å^3	3086.7(1)	1532.3(2)
Z	8	4
D_{calcd}, g cm^{-3}	1.370	1.371
μ(Mo Kα), cm^{-1}	2.14	2.15
T, °C	4	23
λ(Mo Kα), Å	0.71069	0.71069
$R1$ [a]	0.045	0.101
$wR2$ [b]	0.149	0.266

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	1	**2**
Bond Distances		
C(2)–N(1)	1.388(2)	1.283(9)
C(102)–N(11)	1.395(2)	1.284(9)
C(4)–N(1)	1.405(2)	1.430(9)
C(104)–N(11)	1.392(2)	1.410(9)
C(1)–N(2)	1.342(2)	1.321(9)
C(101)–N(12)	1.341(2)	1.325(9)
C(1)–C(2)	1.435(2)	1.452(9)
C(101)–C(102)	1.430(3)	1.493(10)
C(2)–C(3)	1.366(2)	1.453(10)
C(102)–C(103)	1.368(2)	1.447(9)
C(3)–C(103)	1.423(2)	1.341(9)
Bond Angles		
C(1)–C(2)–N(1)	117.0(1)	118.1(6)
C(101)–C(102)–N(11)	117.5(1)	117.8(6)
C(3)–C(2)–N(1)	127.1(1)	126.7(6)
C(103)–C(102)–N(11)	126.5(2)	128.0(7)
C(2)–N(1)–C(4)	126.3(1)	122.0(6)
C(102)–N(11)–C(104)	127.8(1)	121.1(6)

The quinonediimine (**2**) composed of a BT unit is expected to serve as a bidentate ligand using conjugated coordination sites. The preliminary complexation behaviour of **2** was studied. On treatment of **2** in MeCN with a MeCN solution of $Pd(MeCN)_4(BF_4)_2$, the absorption around 430 nm attributable to the charge transfer from the benzenoid moiety to the quinoid moiety disappeared together with appearance of a new band at 492 nm in the UV-vis spectra as shown in Figure 4. The spectral change indicates the coordination of the quinonediimine nitrogens to palladium center. The similar complexation behavior was also observed in the ^{1}H NMR titration experiment. Based on the titration experiment, the 2:1 complex of **2** and a palladium unit was found to be formed to afford the complex **3** (Scheme 1).

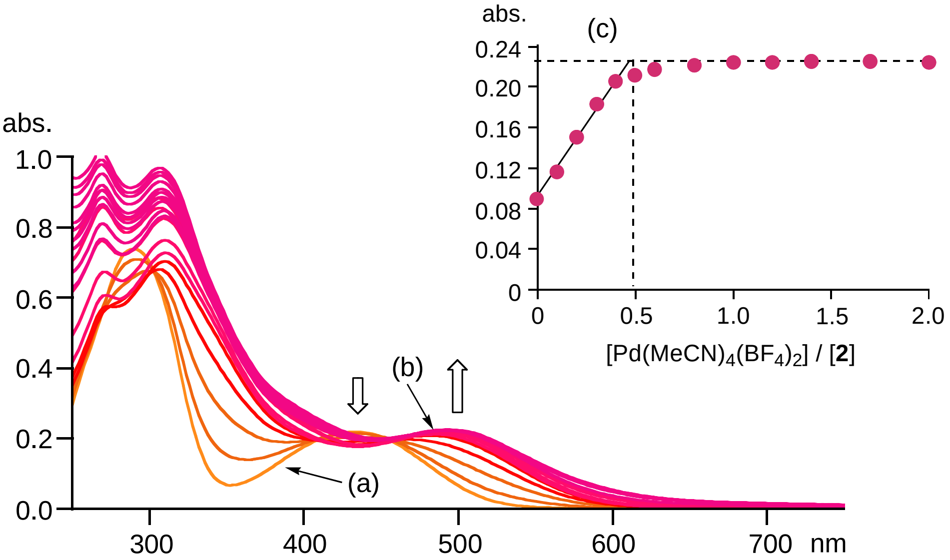
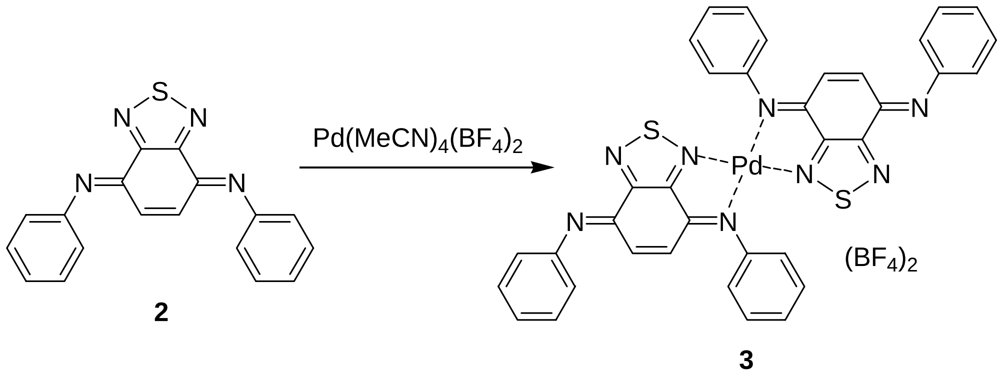
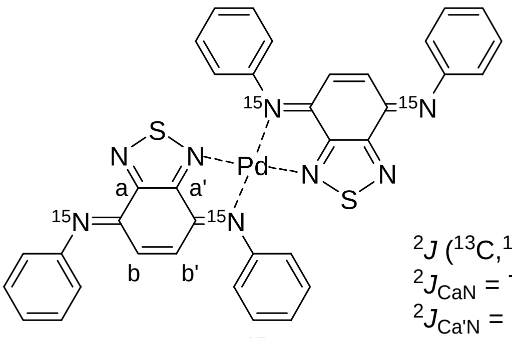


Figure 4. UV-vis. spectra of **2** recorded in MeCN (5.0 x 10^{-5} M) upon the addition of $Pd(MeCN)_4(BF_4)_2$. (a) [**2**] = 5.0 x 10^{-5} M. (b) [2]:$Pd(MeCN)_4(BF_4)_2$ = 2:1. (c) Titration curve for plots of absorbance at 492 nm based on [$Pd(MeCN)_4(BF_4)_2$] / [**2**].



Scheme 1. Complexation of **2** with $Pd(MeCN)_4(BF_4)_2$.

To gain further insight into the complexation behavior, the coupling constants ^2J (^{13}C, ^{15}N) were evaluated. The quinonediimine (**1-^{15}N**) possessing ^{15}N-labeled quinonediimine nitrogens was prepared from $Ph^{15}NH_2$. The coupling constants of ^{15}N with C_a, $C_{a'}$, C_b, and $C_{b'}$ were measured as 7.22, 10.23, 2.41, and 2.40 Hz, respectively (Figure 5). Judging from these values, only one coordination site of **2-^{15}N** is likely to participate in the coordination in *trans* configuration.[33] This finding is in sharp contrast to the complexation of *N,N'*-bis(4'-dimethylaminophenyl)-1,4-benzoquinonediimine, in which both two nitrogen atoms of the quinonediimine moiety coordinate to palladium(II) centers.[31,32] The five-membered chelate coordination of one coordination site of **2** to Pd^{2+} is considered to prevent the incorporation of the second Pd^{2+}. Taking these results into account, the complexation behavior of **2** is reminiscent of a negative allosterism.



3-^{15}N

^2J (^{13}C,^{15}N) values:
$^2J_{CaN}$ = 7.22 Hz, $^2J_{CbN}$ = 2.41 Hz
$^2J_{Ca'N}$ = 10.23 Hz, $^2J_{Cb'N}$ = 2.40 Hz

Figure 5. ^2J (^{13}C, ^{15}N) values of **3-^{15}N**.

CONCLUSION

The aniline oligomers composed of a BT unit were found to adopt the twisted conformation in the crystal state by X-Ray crystallographic analyses. Despite π-conjugation, the *syn*-quinonediimine (**2**) exhibited the more twisted conformation compared with the *syn-p*-phenylenediamine (**1**) which forms intramolecular hydrogen bonds. Furthermore, the BT ring controls the assembled arrangement through π-π interaction in the crystal packing. The controlled complexation of **2** with $Pd(MeCN)_4(BF_4)_2$ was achieved by the *N*-heterocyclic coordination site. This conjugated palladium(II) complex corresponds to a cross-linked polymer complex.[29] The controlled complexation of redox-active π-conjugated molecules or polymers is considered to provide a useful approach to an architechturally ordered arrangement and/or assembly to construct a dimensionally ordered hybrid electronic systems.

EXPERIMENTAL

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. ^1H NMR spectra were recorded on a Varian INOVA 600 (600 MHz) spectrometer with tetramethylsilane as an internal standard. Electronic spectra were obtained by using a Hitachi U-3500 spectrophotometer. Compounds (**1** and **2**) were prepared according to the method reported in a previous paper.[23]

Preparation of Palladium Complex (3)

A mixture of compound (**1**) (31.6 mg, 0.1 mmol) and $Pd(CH_3CN)_4(BF_4)_2$ (22.2 mg, 0.05 mmol) in MeCN (10 mL) was stirred under argon at rt for 12 h. After evaporation of the solution, the palladium complex (**3**) was isolated in 95% yield as yellow powder by reprecipitation from dichloromethane and ether. **3**: IR (KBr): 3067, 1686, 1582, 1482 cm^{-1}. ^{1}H NMR (CD_3CN, 600 MHz) δ 7.84-7.78 (m, 6H), 7.53-7.47 (m, 8H), 7.34 (t, J = 7.2 Hz, 2H), 7.10 (d, J = 10.2 Hz, 2H), 7.00 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 10.2 Hz, 2H).

UV-vis Spectra Measurement

UV-vis spectra were taken under argon atmosphere at 26 °C, using a Hitachi U-3500 spectrophotometer.

X-Ray Structure Analysis

All measurements for **1** and **2** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structures of **1** and **2** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-296877 for **1**, CCDC-296878 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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