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A NOVEL CONDENSED HETEROCYCLIC QUINONE WITH A DIBENZOFURANOBISTHIADIAZOLE SKELETON

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Dedicated to Prof. Dr. Kaoru Fuji on the occasion of his 80th Birthday

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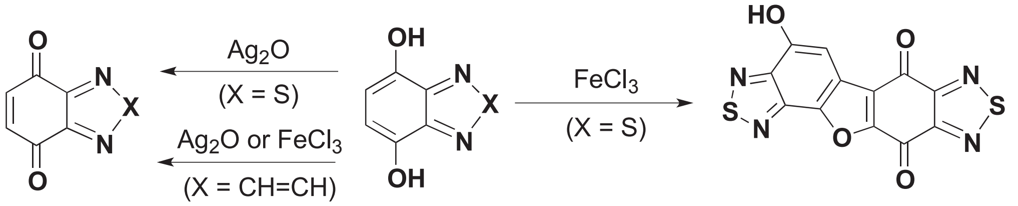
Abstract – Upon oxidation of hydroquinone fused with 1,2,5-thiadiazole by using $FeCl_3$, a novel dibenzofurano[1,2-*c*:6,7-*c'*]bis[1,2,5]thiadiazole-type quinone was obtained whereas the similar dimerization-condensation process did not occur for the pyrazine-fused hydroquinone under the similar conditions.

Quinones consist of an important class of compound undergoing facile electron transfer. The heterocyclic analogues are also attracting from the viewpoint of biological avtivity[1] as well as the important charge-transporting material in the field of organic materials chemistry.[2] The redox reactions of quinones are characterized by the reversible interconversion with the corresponding hydroquinones. However, oxidation of hydroquinone is sometimes accompanied by further reaction of the resulting quinone to give the product with a condensed stucture.[3] Here we report the formation and crystal structure of heterocyclic quinone **1**, the first member of dibenzofurano[1,2-*c*:6,7-*c'*]bis[1,2,5]thiadiazole derivative, which was generated upon oxidation of benzo[1,2-*c*][1,2,5]thiadiazole-4,7-diol **2a**.[4,5]

Previously, the oxidation of hydroquinone **2a** was reported to give the corresponding quinone (*4H*,*7H*-benzo[1,2-*c*][1,2,5]thiadiazole-4,7-dione) **3a**[4,5] when Ag_2O was used as an oxidant. We found here that the reaction of **2a** with $FeCl_3{\bullet}6H_2O$ gave a different product[6] as a dark orange crystalline solid (Scheme 1), which shows C=O stretching frequency characteristic to quinones. Its MS spectral data as well as the elemental analysis indicated that the product has the dimerized structure of **3**. Its structure was finally determined by X-ray analysis[7] to be the five-ring-fused quinone **1**[8] with a hitherto unknown heterocyclic skeleton (Figure 1, Table 1).



3a: X = S
3b: X = CH=CH

2a: X = S
2b: X = CH=CH

1

Scheme 1

Table 1. Selected bond length (Å)[a]

a	1.224(3)	(1.219)
b	1.466(3)	(1.473)
c	1.371(3)	(1.383)
d	1.472(3)	(1.471)
e	1.207(2)	(1.216)
f	1.359(3)	(1.352)

[a] Determined by X-ray analysis at 123K. Values in paranthesis are calculated by DFT method (B3LYP/6-31G*).

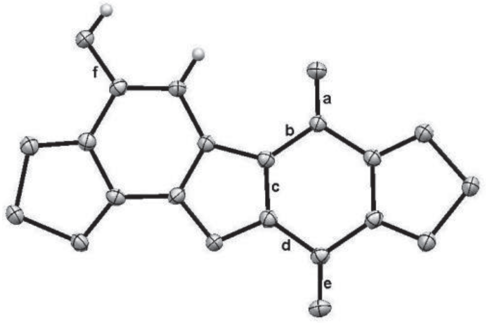


Figure 1. ORTEP drawing of **1**

Because 5,8-hydroxyquinoxaline **2b**,[4] the structurally related another heterocyclic hydroquinone, gave the corresponding quinone **3a** without giving the dimerized product upon oxidation with $FeCl_3{\bullet}6H_2O$[6] or Ag_2O,[4] the observed dimerization-condensation reaction toward the dibenzofuran derivative is affected by the change in the fused heterocycle in **2**. The calculated energy levels (B3LYP/6-31G*) of HOMOs in hydroquinones **2a** (–5.55 eV) and **2b** (–5.50 eV) are nearly the same, which holds true for LUMOs in quinones **3a** (–3.62 eV) and **3b** (–3.52 eV). There are no significant differences in distribution of coefficients (Supplementary Figure S1). Thus, the different behavior by the fused heterocycle upon oxidation of **2** to **3** would not be explained based on the MOs, and still await further examinations (e.g. different coordination behavior of metal to **2** or **3**).

According to the DFT calculation (Figure 2), the hydroxybenzofuran part has large coefficients in HOMO whereas large coefficients are located on the quinone moiety in LUMO. In the crystal, two molecules of **1** are stacked in a face-to-face manner (short C- -C contacts of 3.27 and 3.30 Å; sum of vdW radii: 3.40 Å), suggesting that intermolecular charge-transfer interaction is present in the solid state. Furthermore, the stacked dimers in crystal are further connected by several short intermolecular contacts of S -- N (2.91 Å; sum of vdW radii: 3.35 Å), thus forming ribbon-like network in the solid state (Figure 3). Such interaction has been demonstrated as one of the determinant factors to control the molecular arrangement in crystal.[9,10]

Further studies on this novel heterocyclic quinone **1** are now underway from the both viewpoints of biological and electrochemical aspects.

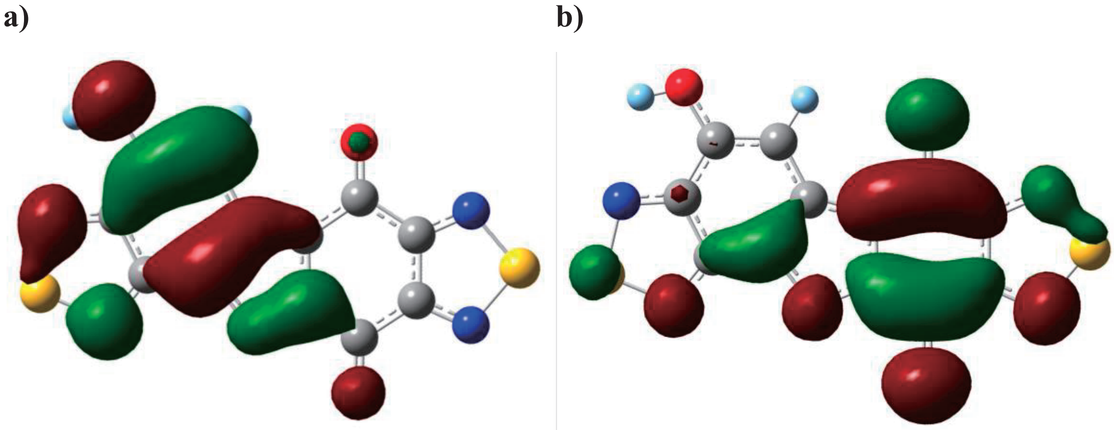


Figure 2. a) HOMO (–6.54 eV) and b) LUMO (–3.51 eV) of **1** calculated by DFT method (B3LYP/6-31G*). Absorption in the visible region (λ_{max} 448 nm in CH_2Cl_2) can be assigned as an intramolecular charge-transfer band.

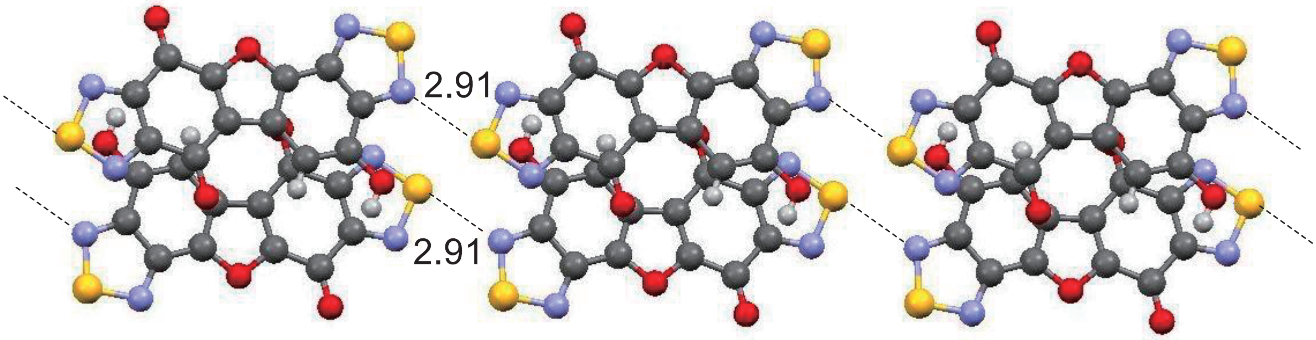


Figure 3. ORTEP drawings of dimeric structure of **1** connected by short S -- N contacts (2.91 Å) into ribbon-like network along the a axis.

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SUPPORTING INFORMATION

Supplementary data (MOs calculated by DFT method) associated with this article can be found, in the online version, at URL: https://wwwheterocycles.jp/newlibrary/downloads/PDFsi/26318/101/1.

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6. Experimental procedure: A solution of **2a** (2.00 g) and $FeCl_3•H_2O$ (6.50 g, 2 eq.) in 100 mL of EtOH was stirred for 1 h at 25 ºC. After concentration and dilution with water, tan precipitates were filtered to give **1** (858 mg, 44%). Analytical sample was obtained as dark orange crystals by sublimation at 290 ºC (10^{-2} Torr). By the similar procedure, **2b** was converted to **3b** in 71% yield.
7. Crystal data of **1**: *MF* $C_{12}H_2O_4N_4S_2$, *FW* 330.29, monoclinic $P2_1/c$ (No. 14), a = 12.5733(2), b = 17.3289(3), c = 5.45596(10), β = 98.6247(16)º, V = 1175.31(4) Å^3, (Z = 4) = 1.866 g cm^{-3}, T = 123 K, R = 5.19%. CCDC 1905132.
8. Data of **1**: mp 355-365 ºC (decomp.); ^{1}H NMR (DMSO-d_6) 7.565 (s, 1H), 11.478 (br. s. 1H) ppm; IR (KBr) 1698, 1665 cm^{-1}; MS (EI) *m/z* 330 (BP); Anal. Calcd for $C_{12}H_2O_4N_4S_2$: C, 43.64; H, 0.61; N, 16.96%. Found: C, 43.80; H, 0.42; N, 17.23%.
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