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First Stable Tetracyanodiphenoquinodimethane with a Completely Planar Geometry: Preparation, X-ray Structure, and Highly Conductive Complexes of Bis[1,2,5]thiadiazolo-TCNDQ

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Abstract

The titled tetracyanodiphenoquinodimethane (TCNDQ) derivative was newly designed and prepared as a novel component for highly conductive organic materials. Introduction of 1,2,5-thiadiazole rings into the TCNDQ skeleton leads to large stabilization in the neutral state. X-ray analysis has revealed their structural details which suggest that interatomic interactions (C-H•••N, S•••N) play an important role in determining the molecular and crystal structure. The novel electron acceptor shows strong electron affinity comparable with that of TCNQ, and gave highly conductive charge-transfer (CT) complexes and an anion radical salt. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical conductors, organic; Quinoid compounds; Thiadiazoles; X-Ray crystal structures

Over the past two decades, much attention has been focused on the development of new building blocks for organic conductors [1]. The fruition of these efforts, involving the discovery of organic superconductors [2], has been mainly brought about by extensive studies on electron donors, however the chemistry of electron acceptors apparently remains still undeveloped. In view of the proposed requirements [3], 13,13,14,14-tetracyanodipheno-quinodimethane (TCNDQ, **1**) derivatives are among the promising acceptors for such purpose. However, few examples [4] have so far appeared in the literature because of the difficulty incurred in thorough investigation of their properties owing to the lack of stability in the neutral state. The instability may come from the twisting about the central double bond due to the repulsion between the biphenylic ortho hydrogens. In order to remove the

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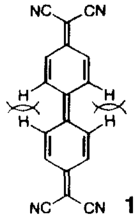
steric interaction, Agranat *et al.* clamped the biphenyl skeleton by two ethylene bridges [5]. Although the resulting tetrahydropyrene derivative **2** thus could be isolated, their structural details were not given. On the basis of these results, we adopted a quite novel approach by fusing extra rings to induce the attractive interaction between the ortho hydrogen and the fused ring. Bi{4*H*,8*H*-4-(dicyanomethylene)benzo[1,2-c:4,5-c′]bis[1,2,5]thiadiazolo-7-ylidene} (**3**) seemed to be a suitable compound to test the validity of our molecular design: first, according to the PM3 calculation (Figure 1), the negative atomic charge is largest at N2 (-0.198) in **3**, leading to considerable stabilization by the electrostatic C-H•••N hydrogen bonding [6], [7] between N2 and the ortho hydrogen; secondly, annelation of the 1,2,5-chalcogenadizole ring [8] dose not induce deformation of the TCNQ skeleton but stabilizes the anionic species by delocalization; thirdly, the intermolecular S•••N≡C interaction in the crystal of **3** would be induced by annelation of the 1,2,5-thiadiazole, which might stabilize the metallic state of the CT complexes or ion radical salts as observed in the bis[1,2,5]thiadiazolo-TCNQ [9]. We report here the preparation, structure, and redox properties of **3** as well as its formation of highly conductive CT complexes.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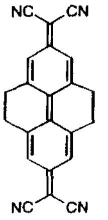
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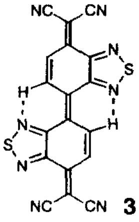
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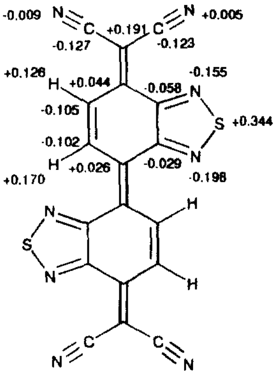
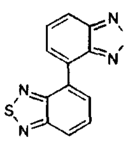


Figure 1. Net atomic charges of **3** calculated by the PM3 method.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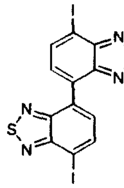
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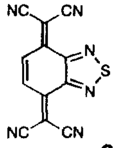
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Reductive coupling of 4-bromobenzo[1,2,5]thiadiazole with Ni(0) catalyst [10] gave **4** [11] in 42% yield, which was converted into the 7,7′-diiodo derivative **5** [12] in 85% yield by treatment with I_2 and Ag_2SO_4 in conc. H_2SO_4 at 110 °C. Pd(0)-catalyzed reaction [13] of **5** with $NaCH(CN)_2$ followed by oxidation of the resulting dianion with Br_2 gave **3** [14] in 22% yield as a sparingly soluble, deep violet solid. The UV/VIS spectrum in CH_2Cl_2 shows no significant absorption except very strong ones at 522 (log ε = 5.11, fwhm = 30 nm) and 488 (4.77, 32 nm) nm, suggesting its conformational rigidity in solution. The new electron acceptor is quite stable in the solid state and also in solution, and its PhCN solution showed no sign of decomposition for several months.

The single crystals of **3** were obtained after many attempts, and X-ray analysis [15] clearly shows that **3** adopts a planar structure (within 0.19 Å deviation) with *trans*-configuration (Figure 2). It is evident that the two short N•••H contacts (2.14 Å; ∠N2•••H2-C4, 129.8°) [7] connect the biphenyl skeleton, and the twisting angle of the central ethylene bond is 0 degree. Furthermore, there is no indication of repulsive force, and the bond lengths and angles around the molecular center fall into the normal values. All the structural features are in agreement with the assumption that the attractive C-H•••N hydrogen bond stabilizes the quinoid system in the neutral form. In the crystal, molecules are connected with four neighbors by another C-H•••N hydrogen bond (2.76 Å; ∠N4•••H2-C4, 138.7°) together with two kinds of S•••N contacts (S1•••N3, 3.35 Å; ∠S1•••N3≡C8, 117.5°: S1•••N1, 3.33 Å; ∠S1•••N1=C1, 159.8°) resulting in the formation of a two-dimensional, coplanar sheet-like structure on the (1 0 -1) plane (Figure 3). These interactions may be helpful in controlling the crystal structure of the anion radical salts or the CT complexes with electron donors.

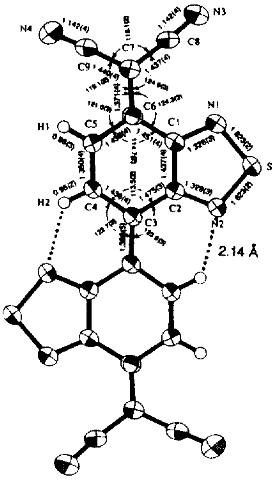

Figure 2. Molecular structure of 3 with the bond distances and selected bond angles. The two molecular halves are related by an inversion center.

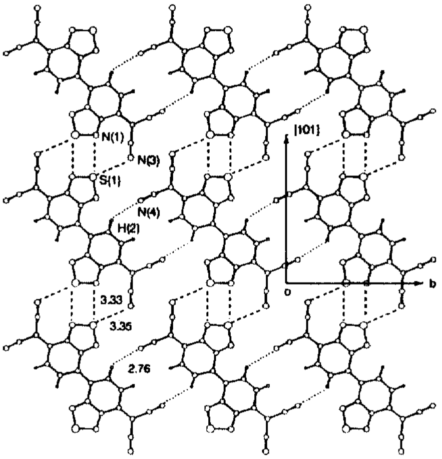

Figure 3. Two-dimensional coplanar sheet-like molecular arrangement in 3. Short interatom contacts of C-H•••N (2.76 Å) and S•••N (3.33, 3.35 Å) are indicated by dotted lines and broken lines, respectively. Perpendicular to this molecular arrangement, the "sheet"s stack to form an infinite multi-layer structure, whereas no efficient molecular overlap is present.

The cyclic voltammogram of 3 shows two reversible one-electron reduction waves. The first reduction potential of 3 (+0.33 V *vs* SCE in CH_2Cl_2) is marginally higher than those of 6 [8] (+0.29 V) and TCNQ (+0.31 V) measured under the same conditions, indicating the strong electron affinity of 3. The well-separated second reduction potential (+0.12 V) indicates the absence of drastic structural change upon one-electron reduction, suggesting the planar geometry for $3^{-\bullet}$. Thus, the anion radical salt $(Bu^n{}_4N^+)_2(3^{-\bullet})_3$ [16] could be isolated upon chemical reduction of 3 with $Bu^n{}_4NI$, which shows good conductivity (1.9 S cm^{-1}) [17]. The smaller difference between E_1 and E_2 in 3 (0.21 V) than in 6 (0.56 V) indicates the large decrease in on-site Coulombic repulsion due to the extension of the π-system. Such redox properties are suitable characteristics for providing highly conductive organic materials. In fact, the 1 : 1 CT complex [16] of 3 with tetrathiafulvalene (TTF) exhibits high electrical conductivity (7.9 S cm^{-1}). Similarly, 3 afforded highly conductive 1 : 1 complexes [16], [17] with bis(ethylenedithio)-TTF (9.8 S cm^{-1}), tetramethyltetraselenafulvalene (18 S cm^{-1}), and tetrathiatetracene (9.9 S cm^{-1}). All the results indicate the validity of our molecular designing, and 3 shows bright prospects for the development of new organic conductors. Further studies are currently in progress.

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[11] **4**: yellow needles; mp 240-241 °C; IR (KBr) ν_{max} 3062, 1530, 1486, 1312, 1145, 869, 856, 815, 804, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (2H, dd, J = 6.8, 1.2 Hz), 8.11 (2H, dd, J = 8.8, 1.2 Hz), 7.80 (2H, dd, J = 8.8, 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$), δ 155.48, 153.59, 130.77, 129.98, 129.43, 121.63; EI-MS (*m/z*, %) 270 (M$^+$, 100); Anal. Calcd for $C_{12}H_6N_4S_2$: C, 53.32; H, 2.24; N, 20.73; S, 23.72. Found: C, 53.57; H, 2.43; N, 20.73; S, 23.87.

[12] **5**: yellow needles; mp 311-312 °C; IR (KBr) ν_{max} 3076, 1560, 1516, 1470, 1315, 1284, 1182, 928, 890, 867, 848, 839, 830, 757 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.30 (2H, d, J = 7.4 Hz), 8.06 (2H, d, J = 7.4 Hz); EI-MS (*m/z*, %) 522 (M$^+$, 100); Anal. Calcd for $C_{12}H_4I_2N_4S_2$: C, 27.61; H, 0.77; N, 10.73; I, 48.61. Found: C, 27.54; H, 0.97; N, 10.52; I, 48.68.

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[14] **3**: deep violet cubes; mp 417 °C (decomp.); IR (KBr) ν_{max} 3113, 2219, 1633, 1563, 1514, 1429, 1316, 1280, 1255, 830 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.84 (2H, d, J = 10 Hz), 7.75 (2H, d, J = 10 Hz) EI-MS (*m/z*, %) 396 (M$^+$, 100); HRMS (*m/z*) 396.0011 (M$^+$; calcd for $C_{18}H_4N_8S_2$, 396.0000); Anal. Calcd for $C_{18}H_4N_8S_2$: C, 54.54; H, 1.02; N, 28.27; S, 16.18. Found: C, 54.65; H, 1.52; N, 28.21; S, 15.64.

[15] Crystal data for **3**: $C_{18}H_4N_8S_2$, M = 396.40, monoclinic $P2_1/c$, a = 7.336 (3), b = 10.601 (1), c = 10.515 (1) Å, β = 101.77 (1)°, V = 800.6 (3) Å^3, D_c (Z = 2) = 1.644 g cm^{-1}, μ (MoKα) = 3.57 cm^{-1}. A total of 1661 unique data ($2\theta_{max}$ = 52°) was collected on a Rigaku AFC-5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) at 13 °C using the ω-2θ scan technique. After absorption correction, the structure was solved by the direct method (SIR92) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the D-map and refined isotropically. The final cycle of full-matrix least-squares refinement was based on 1084 observed reflections [$I > 3\sigma(I)$] and 135 parameters and converged with the R value of 0.034. Residual electron density is 0.15 e Å^{-3}.

[16] The molar ratio was determined in all cases based on the combustion analyses.

[17] All measurements of the electrical conductivities were performed on the compressed powder samples by the four-probe method at room temperature.