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Synthesis and Properties of Benzobis(thiadiazole)s with Nonclassical π-Electron Ring Systems

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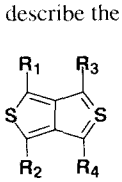
Abstract: Benzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) containing a hypervalent sulfur atom has a low LUMO energy. The aryl derivatives were synthesized using a Stille coupling reaction. The selenadiazole analogues were also prepared. The electron accepting properties of these nonclassical heterocycles were shown by their high reduction potentials. Introduction of electron-donating groups into the electron-withdrawing heterocycles afforded novel donor-acceptor compounds. Their cyclic voltammograms showed that they are easily both oxidized and reduced. Some of them have the absorption maxima above 700 nm due to the small HOMO-LUMO separation. X-ray structure analysis of the diphenyl derivative revealed the formation of a tape-like network through short S···N contacts.

Introduction

Thieno[3,4-*c*]thiophenes (**1**) with a hypervalent sulfur atom have attracted much attention for their interesting structures and reactivities.[1] They are generally unstable and only a few isolable derivatives have been synthesized.[2] Substitution of the thiophene rings by 1,2,5-thiadiazole rings enhances the stability as found in the more stable thieno[3,4-*c*][1,2,5]thiadiazoles (**2**)[3] and [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**3**).[4] Bis([1,2,5]thiadiazolo)[3,4-*b*:3',4'-*e*]pyrazine (**4**) showing high electron affinity was also isolated as a stable crystalline solid where an interesting molecular assembly is formed by short intermolecular heteroatom contacts between the hypervalent S atoms and the N atoms.[5] Furthermore, benzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) derivatives **5** were synthesized and found to show strong electron accepting properties.[6] On the other hand, compounds containing both electron donor and acceptor units are expected to have small HOMO-LUMO gaps which lead to interesting properties such as absorption in near-infrared region,[7] nonlinear optical properties,[8] and single component conductivity.[9] The skeleton of **5** is interesting as an acceptor part of such compounds. If electron donating units are linked to this heterocycle, a new type of donor-acceptor system will be constructed. In these compounds unique molecular networks may be formed by heteroatom contacts as found in **4**. In this report we describe the synthesis and properties of various benzobis(thiadiazole) derivatives **6** and the related



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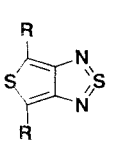

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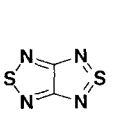

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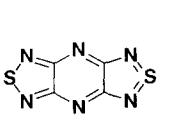

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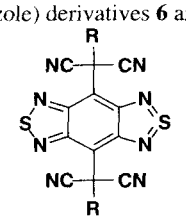
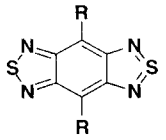
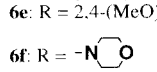


5: R = H, CMe_2CN

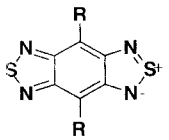


6a: R = H
6b: R = Br
6c: R = Ph
6d: R = *p*-$Me_2NC_6H_4$
6e: R = 2,4-$(MeO)_2C_6H_3$

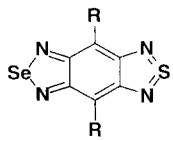


6f: R = -N O

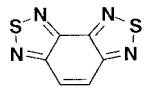
6g: R = SPh



6'



7a: R = H
7b: R = Br
7c: R = Ph



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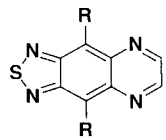


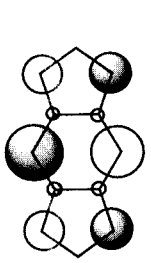
9a: R = H
9b: R = Ph

heterocycles.[10] We also report here novel donor-acceptor compounds containing the nonclassical heterocycles.

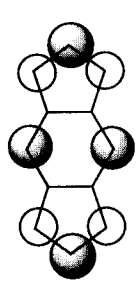
Results and Discussion

Molecular Orbital Calculations

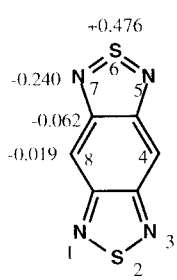
The MNDO-PM3 calculations[11] were performed in order to estimate the properties of nonclassical benzobis(thiadiazole) (**6a**). For comparisons, the calculations of the selenadiazole analogue **7a**, Kekulé-type benzobis(thiadiazole) (**8**) and [1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**9a**) were also carried out. Nonclassical heterocycles **6a** and **7a** have higher HOMO energies and lower LUMO energies than **8** and **9a** (HOMO/eV: **6a**, -8.73; **7a**, -8.73, **8**, -9.94; **9a**, -9.27, LUMO/eV: **6a**, -3.21; **7a**, -3.30; **8**, -1.95; **9a**, -2.39). Therefore, the HOMO-LUMO gaps of **6a** and **7a** are much smaller than those of **8** and **9a**. The HOMO, LUMO, and net atomic charges of **6a** are shown in Figure 1. The 4- and 8-positions of **6a** have large atomic orbital coefficients in the HOMO and LUMO, indicating that introduction of substituents on these positions would have a large effect on the properties. The charge distribution indicates that the sulfur atoms are positively charged, while the nitrogen atoms are negatively charged. This result shows that there is a significant contribution of ylide-type resonance contribution **6'**. For this polarized structure, strong intermolecular interactions through S···N contacts are expected in **6**.



HOMO



LUMO

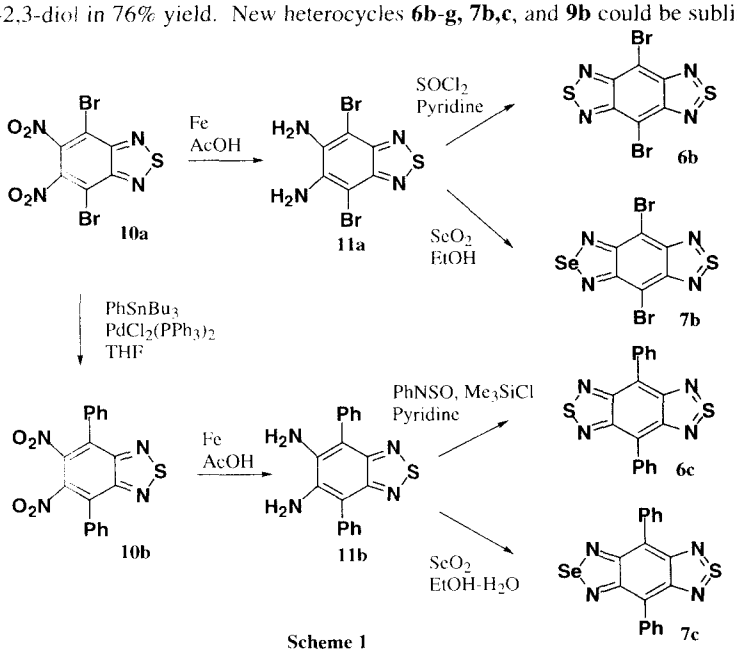


Atomic charges

Figure 1. HOMO, LUMO, and net atomic charges of **6a** calculated by the PM3 method.

Preparation

Nonclassical heterocycles **6b,c** and **7b,c** were synthesized as shown in Scheme 1. Reduction of dibromodinitrobenzothiadiazole (**10a**)[12] with iron dust in acetic acid gave diamine **11a**.[13] Heterocycle **6b** was prepared in 74% yield by reaction of diamine **11a** with thionyl chloride in pyridine at room temperature. The analogous heterocycle **7b** was obtained in 40% yield from diamine **11a** and selenium dioxide. The palladium-catalyzed coupling [$PdCl_2(PPh_3)_2$] of dibromide **10a** with tributylphenyltin[14] in THF afforded **10b**, which was reduced with iron dust to give diamine **11b**. Heterocycle **6c** was prepared in 95% yield by reaction of diamine **11b** with *N*-thionylaniline and trimethysilyl chloride in pyridine at 80 °C. Aryl derivatives **6d,e** were prepared according to the similar method. The selenium compound **7c** was obtained in 82% yield by reaction of **11b** with selenium dioxide. Substitution reaction of dibromide **6b** with morpholine and thiophenol afforded **6f** and **6g**, respectively, although the yields were poor. Quinoxaline derivative **9b** was prepared by reaction of **11b** with 1,4-dioxane-2,3-diol in 76% yield. New heterocycles **6b-g, 7b,c**, and **9b** could be sublimed to purify.



Scheme 1

Properties

The absorption maxima of nonclassical heterocycles **6b-g** and **7b,c** are listed along with **8** and **9b** in Table 1. The values for **6** and **7** are red-shifted compared with those for **8** and **9**. This reflects their smaller HOMO-LUMO gaps suggested by the MO calculations. The selenium analogues **7** show the absorption maxima at longer wavelengths than the corresponding benzobis(thiadiazole)s (**6**), which is regarded as a polar effect caused by the selenium atom. Introduction of donor groups into **6a** raises the HOMO level and makes the absorption maxima more red-shifted. Particularly, compounds **6d** and **6f** containing amino groups showed the absorption maxima in the near-infrared region. The value for dimethoxyphenyl derivative **6e** is close to that for phenyl derivative **6c**. This is attributed to reduction of π-conjugation in the terphenyl unit of **6e** due to the steric hindrance caused by the methoxy substituent at the 2-position of the phenyl group.

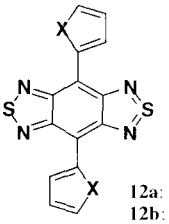
Table 1. Redox Potentials[a] and Absorption Maxima of New Heterocycle

Heterocycle	E^{ox}/V	E^{red}/V	E_1^{ox}-E_1^{red}/V	λ_{max}/nm (log ε)[b]
6b	---	-0.35, -1.10	---	524 (3.64)
6c	---	-0.61, -1.30	---	558 (3.99)
6d	+0.58	-0.75, -1.43[c]	1.33	732 (4.03)
6e	+1.22[c]	-0.74, -1.52[c]	1.96	564 (3.98)
6f	+0.50, +0.28	-0.89, -1.58[c]	1.17	764 (3.70)
6g	+1.28[c]	-0.38, -1.04[c]	1.66	610 (3.90)
7b	---	-0.26	---	609 (---[d])
7c	---	-0.53, -1.21	---	625 (4.01)
8	---	-1.45	---	283 (4.57)
9b	---	-0.82, -1.46	---	471 (3.99)

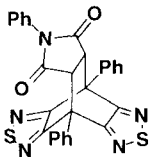
[a] V vs. SCE, 0.1 mol dm^{-3} Bu_4NClO_4 in CH_2Cl_2. [b] In CH_2Cl_2. [c] Irreversible wave. [d] Not obtained because of its low solubility.

Heterocycles **6**, **7** and **9b** display strong emission. The fluorescence spectra of **6b**, **6c**, **7b**, **7c** and **9b** were measured upon photoexcitation in dichloromethane at room temperature. They showed the following emission maxima: **6b**; 557 nm, **6c**; 642 nm, **7b**; 643 nm, **7c**; 689 nm, **9b**; 561 nm.

The cyclic voltammetry (CV) of **6b,c** and **7c** in dichloromethane showed two reversible one-electron reduction waves. The reduction potentials are shown in Table 1. The first reduction potentials of these heterocycles are comparable to that of *p*-benzoquinone (E_1^{red} = -0.46 V), indicating their high electron affinity. The electron-withdrawing bromo groups at the 4- and 8-positions further increase the reduction potentials. Kekulé-type benzobis(thiadiazole) (**8**) and pyrazine derivative **9b** show lower reduction potentials. This fact indicates that the high electron affinity of **6** and **7** is attributable to the 14π-electron ring system containing a hypervalent sulfur atom, which generates a more stable Kekulé-type thiadiazole upon accepting an electron. This result is in accord with the MO calculations showing that the LUMO levels of nonclassical heterocycles are lower than those of Kekulé-type heterocycles. Selenadiazole analogue **7c** shows a little higher reduction potentials than **6c** due to the lower LUMO level. Compounds **6d-g** containing electron-donating groups showed oxidation potentials in addition to reduction potentials. The differences between the first oxidation potentials and the first reduction potentials (E_1^{ox} - E_1^{red}) are well correlated with the HOMO-LUMO gaps determined by the absorption spectra. In **6d** and **6f**, these values are significantly small, indicating that they are good amphoteric redox systems. We have recently prepared benzobis(thiadiazole)s **12a,b** containing thiophene and *N*-methylpyrrole.[15] Since these five-membered heterocycles are good electron donors, they have small HOMO-LUMO gaps and the absorption maxima were observed at 702 and 694 nm, respectively. The oxidation potentials of **6d** and **6f** having amino groups are very low, indicating that they are strong electron donors. Therefore, they may be used as electron donors for affording organic conductors.



12a: X = S
12b: X = NMe



13

X-ray Structure Analysis

In order to investigate molecular and crystal structures of the nonclassical benzobis(thiadiazole)s (**6**), X-ray structure analyses of **6b** and **6c** were carried out.[16] The single crystals of **6b** and **6c** were obtained by recrystallization from benzonitrile and toluene, respectively. The molecules of **6b** and **6c** are centrosymmetric. The S-N bond lengths (1.601 and 1.603 Å in **6b**, 1.597 and 1.606 Å in **6c**) are shorter than those of Kekulé-type compound **8** (1.615 and 1.620 Å)[17] and longer than the S-N double bond of sulfur diimide (1.53 Å).[18] The N-C bond lengths (1.354 and 1.357 Å in **6b**, 1.377 and 1.378 Å in **6c**) are longer than those of **8** (1.347 and 1.370 Å). The bond lengths of the thiadiazole rings of **6b** and **6c** are similar to those of the pyrazine derivative **4** (S-N bond lengths: 1.597 and 1.609 Å, N-C bond lengths: 1.347 and 1.370 Å).[5] This result indicates the hypervalency on the sulfur atoms of **6**. Although the benzobis(thiadiazole) moiety is planar, the plane of the two phenyl groups of **6c** twists with the dihedral angle of 45.9 ° from the planar heterocyclic unit. The molecules of **6c** form a tape-like network by short S···N contacts (3.26 Å) as shown in Figure 2(a). The S···N interactions are considered to be due to an electrostatic effect since the S atoms are positively and the N atoms are negatively charged. In this crystal lattice, toluene molecules are incorporated. The molecules of **6c** are uniformly stacked as shown in Figure 2(b), where the distances between the molecular planes are 3.45 and 3.57 Å. The crystal structure of **6b** is more complex than that of **6c**, where tape-like networks formed by S···N contacts (3.10 Å) are linked by Br···N contacts (3.10 Å).[10]

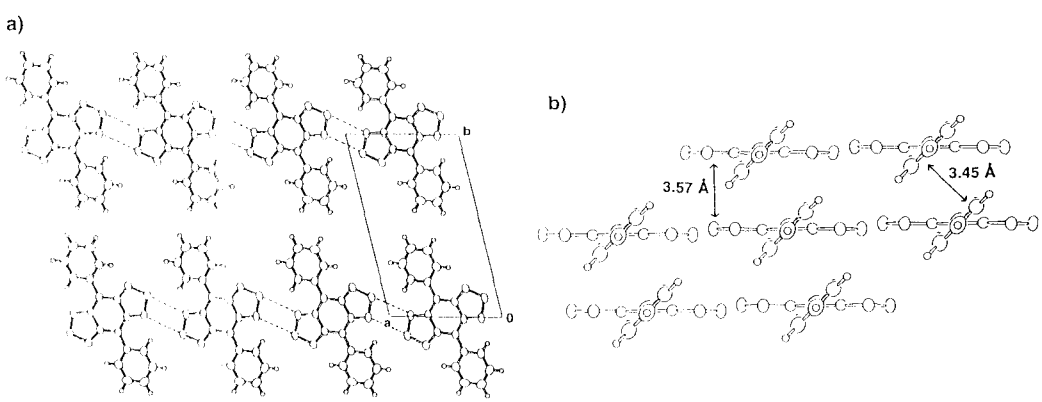


Figure 2. Crystal structure of **6c**, a) tape-like network, broken line S···N contacts (3.26 Å), b) stacking mode.

Diels-Alder Reaction

Heterocycles containing a nonclassical thiophene ring are highly reactive and some Diels-Alder reactions with dienophiles have been reported.[1] Benzobis(thiadiazole)s (**6**) were also expected to undergo the Diels-Alder reaction with dienophiles. When **6c** was heated with *N*-phenylmaleimide in refluxing xylene, a 1:1 adduct **13** was obtained in 89% yield. Although the product dissociated to the starting materials in the EI mass measurement, the FAB mass spectrum showed the molecular weight for the 1:1 adduct. It is reasonable that **6c** reacts with a dienophile at the 4- and 8-positions because of the large atomic coefficients at these positions in the HOMO as shown in Figure 1. The adduct **13** reverted to **6c** and *N*-phenylmaleimide by a retro-Diels-Alder reaction at its decomposition point (> 230 °C). Since the color drastically changes from colorless to violet upon heating, **13** is of interest as a functional dye.

Conclusion

Novel heterocycles **6** and **7** containing a hypervalent sulfur atom were synthesized and characterized. In the synthesis a Stille coupling reaction was useful for the introduction of aryl groups. The nonclassical heterocycles **6** and **7** have higher electron affinity and smaller HOMO-LUMO gaps than the corresponding Kekulé-type compounds. These properties were shown by the absorption spectra and the redox potentials, and were supported by the PM-3 calculations. These heterocycles show strong fluorescence emission and may be applicable for organic electroluminescence devices. The derivatives containing electron-donating groups show amphoteric redox properties which were tunable by the substituents. X-ray structure analyses of **6b** and **6c** revealed that tape-like molecular networks are formed by short S···N contacts. This intermolecular interaction may be used to construct unique molecular assemblies.

Experimental

Melting points were measured on a YANACO MP-500D melting point apparatus and are uncorrected. IR spectra were determined on a PERKIN-ELMER FTIR 1600 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained using a JEOL JNM-GX400 (400 MHz) spectrometer. Mass spectra (EI) were obtained with a SHIMADZU GCMS-QP1000EX mass spectrometer operating at 70 eV by a direct inlet system. High resolution mass spectra (EI) and a FAB mass spectrum (Xe, 7 kV) using *m*-nitrobenzyl alcohol as a matrix were measured on a SHIMADZU KRATOS CONCEPT 1S mass spectrometer. UV/Vis absorption spectra and fluorescence spectra were determined on SHIMADZU UV-3101PC and SHIMADZU RF-1500 spectrometers, respectively. Elemental analyses were performed on a YANACO MT-3 CHN CORDER. Purification on column chromatography was performed using MERCK silica gel 60 (63-200 μm) or MERCK aluminum oxide 90 (activity I, neutral). All solvents were dried and purified by the usual methods.

General Procedure for Preparation of Aryltributyltin. Magnesium ribbon (1.46 g) in dry THF (30 mL) was activated with ultrasonic waves for 3 min under argon. A small amount of aryl bromide was added to the magnesium. After a reaction occurred exothermically, a solution of aryl bromide (50 mmol) in THF (20 mL) was added dropwise over 2 h. Then, to the Grignard reagent was slowly added a solution of tributyltin chloride (10.28 g, 30 mmol) in THF (20 mL) over 2 h, and the mixture was refluxed for 18 h. The reaction mixture was slowly poured into water (500 mL) and the solution was extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was distilled at a reduced pressure using a Kugelrohr distillation apparatus to give the product.

5,6-Dinitro-4,7-diphenylbenzo[*c*][1,2,5]thiadiazole (10b). To a mixture of dibromide **10a** (1.50 g, 3.9 mmol) and $PdCl_2(PPh_3)_2$ (0.55 g, 0.78 mmol) was added a solution of tributylphenyltin (3.15 g, 8.6 mmol) in dry THF (20 mL) under argon. The mixture was refluxed for 4 h, and then stirred with aqueous KF solution. Dichloromethane (50 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic solution was washed with aqueous NaCl solution and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel (dichloromethane/n-hexane, 1:1) to give **10b** (0.97 g, 65%) as pale yellow prisms: mp 295-296 °C (from toluene); IR (KBr) 1552, 1382, 1356, 890, 753, 699 cm^{-1}, ^1H NMR (DMSO-d_6) δ 7.61 (s, 10 H); ^{13}C NMR (DMSO-d_6) δ 128.9, 129.16, 129.22, 130.1, 130.9, 141.3, 152.8; MS *m/z* (relative intensity) 378 (M^+, 54), 301 (35), 77 (100). Anal. Calcd. for $C_{18}H_{10}N_4O_4S$: C, 57.14; H, 2.66; N, 14.81. Found: C, 57.42; H, 2.95; N, 14.87.

5,6-Diamino-4,7-diphenylbenzo[*c*][1,2,5]thiadiazole (11b). A mixture of **10b** (1.32 g, 3.5 mmol) and iron powder (1.95 g, 35 mmol) in acetic acid (20 mL) was heated at 100 °C for 1.5 h under nitrogen. After cooling, the precipitate was filtered and washed with methanol. The resulting solid was dissolved into hot ethyl acetate. The hot solution was treated with activated carbon and filtered. The filtrate was cooled to give **11b** (0.74 g, 67%) as yellow needles: decomp 307-308 °C (from ethyl acetate); IR (KBr) 3423, 3324, 3239, 1636, 1456, 1432, 1365, 880, 824, 756, 700, 650, 518 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5,35 (br s, 4 H, NH_2), 7.40-7.44 (m, 2 H), 7.48-7.56 (m, 8 H); ^{13}C NMR (DMSO-d_6) δ 109.1, 127.3, 128.9, 130.6, 135.7, 138.8, 150.6; MS *m/z* (relative intensity) 318 (M^+, 100), 317 (42). Anal. Calcd. for $C_{18}H_{14}N_4S$: C, 67.90; H, 4.43; N, 17.60. Found: C, 68.00; H, 4.61; N, 17.61.

4,8-Dibromobenzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (6b). To a solution of diamine **11a** (0.33 g, 1.0 mmol) in dry pyridine (5 mL) was added thionyl chloride (1 mL) under argon. The reaction mixture was stirred for 20 h at room temperature. After removal of the solvent at a reduced pressure, water was added to the residue. The precipitate was filtered and washed with water and methanol. The crude product was sublimed at 200 °C under 10^{-6} Torr to give **6b** (0.26 g, 74%) as deep red crystals: decomp > 280 °C; IR (KBr) 1459, 1280, 1264, 924, 854, 604, 472 cm^{-1}; UV (CH_2Cl_2) λ_{max} 524 nm (log ε 3.64), 359 (4.26), 239 (4.33); MS *m/z* (relative intensity) 354 (55), 352 (M^+, 100), 350 (47), 273 (31), 271 (28), 192 (53), 96 (40), 70 (85). Anal. Calcd. for $C_6Br_2N_4S_2$: C, 20.47; N, 15.92. Found: C, 20.74; N, 16.10.

4,8-Diphenylbenzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (6c). A mixture of diamine **11b** (1.00 g, 3.1 mmol) and *N*-thionylaniline (0.74 mL, 6.5 mmol) in dry pyridine (12 mL) was stirred at 80 °C under argon. After stirring for 5 min, trimethylsilyl chloride (4 mL, 31 mmol) was added, and the reaction mixture was stirred for 5 h at the same temperature. The solvent was distilled off at a reduced pressure, and dichloromethane (50 mL) was added to the residue. The solution was washed with 1*N* hydrochloric acid, aqueous $NaHCO_3$ solution, and water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was chromatographed on silica gel (toluene) to give **6c** (1.02 g, 95%) as purple prisms: decomp 310-311 °C (sublimation at 200 °C, 10^{-6} Torr); IR (KBr) 1449, 1364, 935, 868, 755, 687, 667, 506 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54-7.58 (m, 2 H), 7.66 (t, J = 7.6 Hz, 4 H), 8.20 (d, J = 7.6 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 121.6, 128.3, 129.0, 131.6, 134.9, 152.7; UV (CH_2Cl_2) λ_{max} 558 nm (log ε 3.99), 359 (4.33), 291 (4.25), 243 (4.30); MS *m/z* (relative intensity) 346 (M^+, 100), 313 (38). Anal. Calcd. for $C_{18}H_{10}N_4S_2$: C, 62.40; H, 2.91; N, 16.18. Found: C, 62.67; H, 3.11; N, 15.97.

Similarly to the synthesis of **6c**, **6d** and **6e** were prepared. **6d**: decomp 301-303 °C; IR (KBr) 1604, 1428, 1373, 1206, 1135, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.10 (s, 12 H), 6.97 (d, J = 8.9 Hz, 4 H), 8.23 (d, J = 8.9 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 40.2, 111.9, 119.9, 123.5, 132.7, 150.5, 152.7; UV (CH_2Cl_2) λ_{max} 732 nm (log ε 4.03), 355 (4.42), 345 (4.41), 264 (4.12); MS *m/z* (relative intensity) 432 (M^+, 100), 417 (16), 216 (23). Anal. Calcd. for $C_{22}H_{20}N_6S_2$: C, 61.08; H, 4.66; N, 19.43. Found: C, 61.11; H, 4.72; N, 19.38. **6e**: decomp 322-326 °C; IR (KBr) 1609, 1576, 1467, 1309, 1213, 1166, 1116, 1044, 1030, 921, 615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.76 (s, 3 H), 3.77 (s, 3 H), 3.94 (s, 6H), 6.75-6.79(m, 4 H), 7.54-7.59 (m, 2 H); UV (CH_2Cl_2) λ_{max} 564 nm (log ε 3.98), 357 (4.41), 287 (4.27), 240 (4.47); MS *m/z* (relative intensity) 466 (M^+, 100), 343 (35). Anal. Calcd. for $C_{22}H_{18}N_4O_4S_2$: C, 56.63; H, 3.89; N, 12.01. Found: C, 56.77; H, 3.86; N, 12.14.

4,8-Bis(4-morpholino)benzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (6f). To a solution of dibromide **6b** (35 mg, 0.10 mmol) in dimethylformamide (3 mL) was added morpholine (0.1 mL) at 80 °C under argon. The green solution was stirred for 25 min. The solvent was distilled off at a reduced pressure. Water was added, and the resulting precipitate was filtered. After drying in *vacuo*, the solid was sublimed at 170 °C and 10^{-6} Torr to give **6f** (4 mg, 10%) as a green solid: decomp > 180 °C; IR (KBr) 2872, 1460, 1433, 1368, 1277, 1120, 1105, 1003, 930, 871, 863, 563 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.64-3.68 (m, 8H), 4.09-4.10 (m, 4H), 4.56-4.58 (m, 4H); UV (CH_2Cl_2) λ_{max} 764 nm (log ε 3.70), 350 (4.28), 277 (4.49); MS *m/z* (relative intensity) 364 (M^+, 100). Mass. Calcd. for $C_{14}H_{16}N_6O_2S_2$: 364.07762. Found: *m/z* 364.07913

4,8-Bis(phenylthio)benzo[1,2-*c*:4,5-*c*']bis([1,2,5]thiadiazole) (6g). To a solution of dibromide **6b** (32 mg, 0.09 mmol) in dimethylformamide (2 mL) was added thiophenol (20 μL, 0.2 mmol) at 80 °C under argon. After stirring for 1 h, the reaction mixture was further stirred for 1h with additional thiophenol (20 μL, 0.2 mmol). After removal of the solvent, the residue was washed with n-hexane, ether, and methanol. The resulting precipitate was filtered and washed with methanol. The solid was sublimed at 200 °C and 10^{-6} Torr to give **6g** (4 mg, 11%) as a blue-black solid: decomp 237-238 °C; IR (KBr) 1578, 1477, 1437, 1294, 1022, 930, 878, 855, 737, 696, 687, 634, 531, 490 cm^{-1}; UV (CH_2Cl_2) λ_{max} 610 nm (log ε 3.90), 356 (4.36), 283 (4.21), 249 (4.42); MS *m/z* (relative intensity) 410 (M^+, 100), 377 (13), 333 (13), 301 (37). Mass. Calcd. for $C_{18}H_{10}N_4S_4$: 409.97884. Found: *m/z* 409.97741.

4,8-Diphenyl[1,2,5]selenadiazolo[3,4-*f*]benzo[*c*][1,2,5]thiadiazole (7b). A mixture of diamine **11a** (65 mg, 0.20 mmol) and selenium dioxide (55 mg, 0.50 mmol) in ethanol (10 mL) was refluxed for 24 h. The precipitate was filtered and washed with hot water and hot ethanol. Purification by sublimation (220 °C, 10^{-6} Torr) afforded **7b** (32 mg, 40%) as purple crystals: decomp > 280 °C; IR (KBr) 1451, 1351, 1276, 921, 860, 808, 756, 598 cm^{-1}; UV (CH_2Cl_2) λ_{max} 609 nm (log ε 4.01), 383, 250; MS *m/z* (relative intensity) 402 (53), 400 (M^+, 97), 398 (85), 319 (38), 240 (59), 238 (31), 177 (26), 175 (33), 96 (70), 80 (100), 70 (88). Anal. Calcd. for $C_6Br_2N_4SSe$: C, 18.06; N, 14.05. Found: C, 18.16; N, 13.98.

4,8-Diphenyl[1,2,5]selenadiazolo[3,4-*f*]benzo[*c*][1,2,5]thiadiazole (7c). A mixture of diamine **11b** (64 mg, 0.20 mmol) and selenium dioxide (22 mg, 0.20 mmol) in a solution of ethanol (7 mL) and water (3 mL) was refluxed for 15 min. After cooling, the precipitate was filtered and washed with water and methanol. Purification by column chromatography on silica gel (dichloromethane) and sublimation (220 °C, 10^{-6} Torr) afforded **7c** (65 mg, 82%) as blue crystals: decomp 367-371 °C; IR (KBr) 1446, 1433, 1371, 940, 874, 834, 763, 751, 700, 685, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53-7.57 (m, 2 H), 7.63-7.67 (m, 4H), 8.10-8.13 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 121.6, 128.2, 128.9, 131.8, 135.7, 152.8, 158.8; UV (CH_2Cl_2) λ_{max} 625 nm

(log ε 4.01), 380 (4.46), 299 (4.29), 264 (4.13), 226 (4.27); MS *m/z* (relative intensity) 394 (M^+, 41), 392 (22), 314 (100). Anal. Calcd. for $C_{18}H_{10}N_4SSe$: C, 54.96; H, 2.56; N, 14.25. Found: C, 55.13; H, 2.81; N, 14.10.

4,9-Diphenyl[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (9b). A solution of diamine **11b** (70 mg, 0.22 mmol) and 1,4-dioxane-2,3-diol (130 mg, 1.1 mmol) in nitromethane (3 mL) was refluxed for 2 h under argon. After cooling, the orange precipitate was filtered and washed with nitromethane. The resulting solid was sublimed at 240 °C under 10^{-6} Torr to give **9b** (57 mg, 76%) as orange crystals: decomp > 373 °C; IR (KBr) 1459, 1442, 1389, 1040, 897, 861, 756, 698, 652, 455 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55-7.58 (m, 2 H), 7.64 (t, J = 7.6 Hz, 4 H), 7.85 (t, J = 7.6 Hz, 4 H), 8.87 (s, 2H); UV (CH_2Cl_2) λ_{max} 471 nm (log ε 3.99), 363 (4.26), 349 (4.14), 254 (4.74); MS *m/z* (relative intensity) 340 (M^+, 100), 339 (77), 306 (71). Anal. Calcd. for $C_{20}H_{12}N_4S$: C, 70.56; H, 3.55; N, 16.46. Found: C, 70.41; H, 3.85; N, 16.47.

Diels-Alder Reaction of 6c with *N*-phenylmaleimide. A mixture of **6c** (176 mg, 0.51 mmol) and *N*-phenylmaleimide (173 mg, 1.0 mmol) in *o*-xylene (5 mL) was refluxed for 2 d under nitrogen. After cooling, the reaction mixture was separated by column chromatography on silica gel to give an adduct **13** (eluent CH_2Cl_2). Recrystallization from n-hexane gave **13** as colorless needles (215 mg, 89%) containing 28% of CH_2Cl_2: decomp > 230 °C; IR (KBr) 1716, 1499, 1378, 1192, 753, 691, 651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.40 (s, 2H), 5.25 (s, 0.55H, CH_2Cl_2), 6.63-6.66 (m, 2H), 7.20-7.22 (m, 3 H), 7.52 (t, J = 7.5 Hz, 2 H), 7.61 (t, J = 7.5 Hz, 4 H), 8.15 (d, J = 7.5 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 49.7, 55.3, 125.8, 128.3, 128.8, 128.9, 129.2, 130.4, 131.3, 161.5, 163.6, 170.2; UV (CH_2Cl_2) λ_{max} 279 nm (log ε 4.30), 225 (4.12); FAB-MS *m/z* 520 $(M + H)^+$. Anal. Calcd. for $C_{28}H_{17}N_5O_2S_2$: C, 64.72; H, 3.30; N, 13.48. Found: C, 64.63; H, 3.43; N, 13.29 (dried in *vacuo* at 110 °C for 7 h).

X-ray Structure Analysis of 6c. A deep purple crystal having approximate dimensions of 0.50 x 0.20 x 0.05 mm was prepared by recrystallization from toluene. A Rigaku AFC7R diffratometer was used with graphite-monochromated Mo Kα radiation, ω–2θ scan technique. Crystal data are as follows: MF $C_{18}H_{10}N_4S_2(C_7H_8)_{0.5}$, MW 438.56, triclinic, space group $P\bar{1}$, a = 8.605 (2) Å, b = 14.203(4) Å, c = 3.816(1) Å, α = 95.61(3)°, β = 100.52(3)°, γ = 75.51(2)°, V = 443.3(2) $Å^3$, Z = 1, D_{calcd} = 1.64 g/cm^3. A total of 2017 unique data was collected up to $2\theta_{max}$ = 55° at 296 K. The structure was solved by the direct method using the SHELXS86 program. The non-hydrogen atoms were refined anitsotropically by the full-matrix least-squares method. Hydrogen atoms were included at calculated positions but not refined. The final R and R_w values are 0.065 and 0.069 for 1296 reflections with $|F_o| > 3\sigma|F_o|$. All calculations were performed using teXsan crystallographic software package of Molecular Structure Corporation.

Electrochemical Measurements. Cyclic voltammetry was performed on a TOHO TECHNICAL RESEARCH Polarization Unit PS-07 potentiostat / galvanostat. The electrochemical measurements were carried out in distilled dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate using Pt working and counter electrode and a standard calomel electrode (SCE). The concentration of each sample was ca. 0.5 mmol dm^{-3}. The solution was degassed by argon bubbling. The scan rate was 100 mV s^{-1}. All values are given in V vs. SCE.

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