

HETEROCYCLES, Vol. 71, No. 2, 2007, pp. 253 - 268. © The Japan Institute of Heterocyclic Chemistry  
Received, 28th, July, 2006, Accepted, 22nd December, 2006, Published online, 26th December, 2006. COM-06-10848

## **SYNTHESES, STRUCTURES, AND SPECTROSCOPIC PROPERTIES OF PUSH-PULL HETEROQUINOID COMPOUNDS**

**Shinobu Inoue,<sup>†</sup> Shinji Mikami,<sup>†</sup> Kazuo Takimiya,<sup>†</sup> Tetsuo Otsubo,<sup>†\*</sup> and  
Yoshio Aso<sup>‡</sup>**

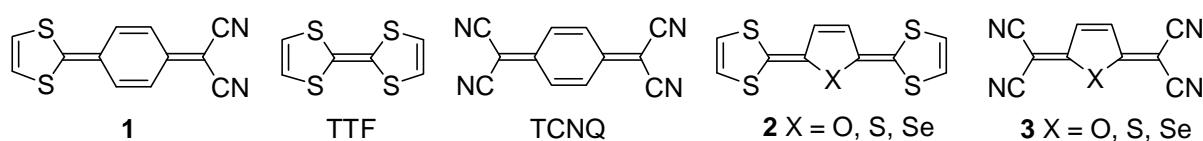
<sup>†</sup>Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan and <sup>‡</sup>The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan; E-mail [otsubo@hiroshima-u.ac.jp](mailto:otsubo@hiroshima-u.ac.jp)

**Abstract** – A variety of push-pull heteroquinoid compounds (**4–10**) bearing an electron-donating 1,3-dithiol-2-ylidene group and an electron-accepting dicyanomethylene group were prepared by the coupling reactions of the corresponding dicyanomethyl heteroaromatics with 2-methylthio-1,3-ditholium methyl sulfate according to the Gompper method. All these compounds are highly colored and amphoteric. The electronic absorption spectra have revealed that their deep colors arise from a strong intramolecular charge-transfer absorption band in the visible region. The infrared nitrile vibrational spectra have indicated that these molecules exist as a resonance hybrid of the quinoid and zwitterionic forms, accordingly, assuming considerably polarizable characters. The amphoteric and polarizable characters of the simple heteroquinoid compounds (**4–7**) are nearly independent of the kind of the constituent chalcogen atom and of the introduction of the octylthio or hexyl groups into the frameworks. On the other hand, those of the extensive heteroquinoid compounds (**8–10**) are largely enhanced because of increasing gain in aromaticity of the heterocyclic rings in the zwitterionic form.

### **INTRODUCTION**

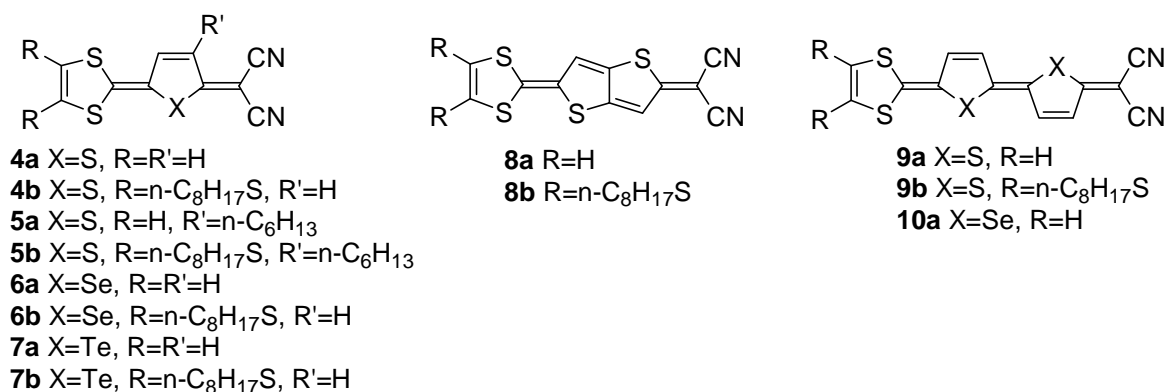
A push-pull type or donor-acceptor type of organic compounds have attracted current interest from the standpoint of advanced optoelectronic materials, such as highly colored dyes<sup>1,2</sup> and nonlinear optics.<sup>3,4</sup> These compounds can be usually designed by installing an electron-donating group at the terminal position and an electron-accepting group at the opposite terminal position of conjugated aromatic, olefinic, acetylenic, or quinoid frameworks. Among them, interesting are the push-pull benzoquinoid compound

(1) and related compounds, originally developed by Gompper and coworkers (Scheme 1).<sup>5</sup> Compound (1) bearing 1,3-dithiol-2-ylidene as a strong electron-donating group and dicyanomethylene as a strong electron-accepting group is formally regarded as a structural hybrid of TTF and TCNQ. Thanks to the strong amphoteric framework, it is highly colored and polarizable.<sup>6</sup> The extended 1,4-naphthoquinoid,<sup>5</sup> 9,10-anthraquinoid,<sup>5</sup> and biphenoquinoid<sup>7</sup> analogues of 1 were also revealed to show intriguing optical properties derived from individual amphotericity.



**Scheme 1.** Structures of quinoid molecules.

Versatile heteroquinoid frameworks have been successfully utilized in the designs of TTF-type electron donors such as 2<sup>8</sup> and TCNQ-type electron acceptors such as 3,<sup>9,10</sup> resulting in the developments of numerous novel organic conductors among their molecular complexes. This has directed our interest towards push-pull heteroquinoid analogues of 1. In this paper, we would like to report the syntheses, structures, and spectroscopic properties of a wide variety of the heteroquinoid compounds (4–10) as novel optoelectronic materials (Scheme 2).<sup>11,12</sup>

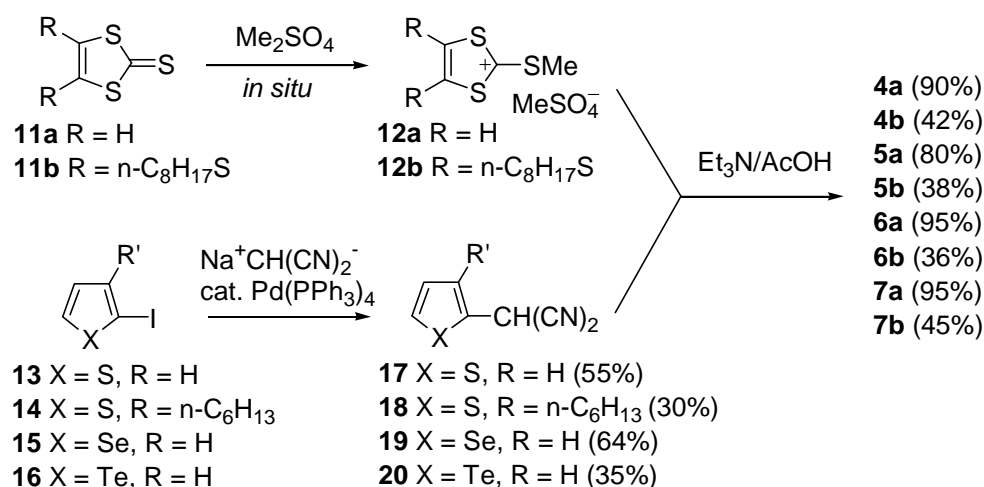


**Scheme 2.** Structures of push-pull heteroquinoid molecules

## RESULTS AND DISCUSSION

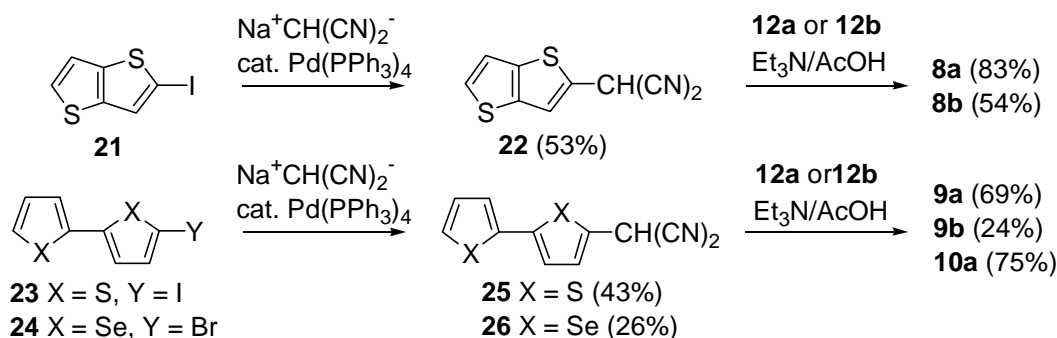
**Synthesis.** All the push-pull heteroquinoid compounds (4–10) were readily prepared by the Gompper coupling reactions<sup>5</sup> of appropriate dicyanomethyl heteroaromatics and 2-methylthio-1,3-dithiolium methyl sulfate. In the synthesis of 4a, as demonstrated in Scheme 3, 2-dicyanomethylthiophene (17) was first prepared by a substitution reaction of 2-iodothiophene (13) with sodium dicyanomethanide according to the Takahashi protocol.<sup>13,14</sup> The subsequent CN coupling of 17 with 2-methylthio-1,3-dithiolium methyl sulfate (12a),<sup>15</sup> *in situ* generated by treating 1,3-dithiole-2-thione (11a) with dimethyl sulfate in

acetic acid, in the presence of triethylamine at 110 °C gave the desired push-pull thienoquinoid compound (**4a**) in 90% yield. Similar reactions of 2-dicyanomethyl-5-hexylthiophene (**18**), 2-dicyanomethylselenophene (**19**), and 2-dicyanomethyltellurophene (**20**) with **12a** also gave the heteroquinoid compounds (**5a**, **6a**, and **7a**), respectively, in excellent yields. On the other hand, the coupling reactions of **17–20** with 4,5-bis(octylthio)-2-methylthio-1,3-dithiolium methyl sulfate (**12b**) reluctantly proceeded to afford the octylthio-substituted derivatives (**4b**, **5b**, **6b**, and **7b**) in markedly reduced yields (36–45%).



**Scheme 3.** Synthesis of push-pull heteroquinoid compounds (**4–7**).

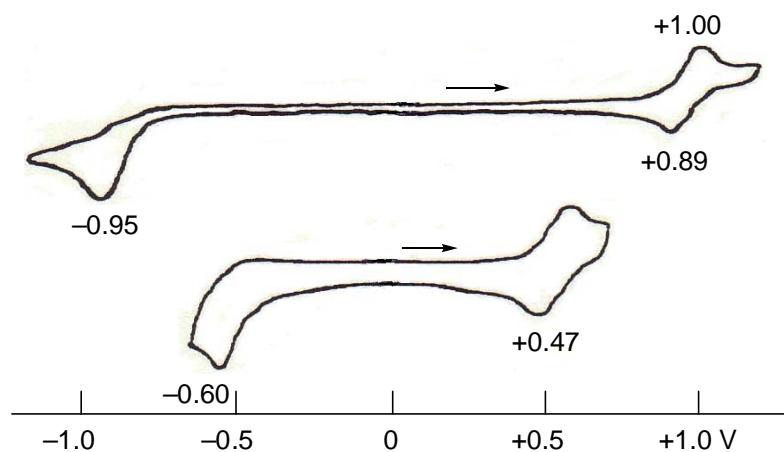
The extended heteroquinoid compounds (**8a,b**, **9a,b** and **10a**) were similarly prepared from the corresponding dicyanomethylheteroaromatics (**22**, **25**, and **26**) (Scheme 4). The successful preparations of these extended compounds by the Gompper method are ascribable to high nucleophilicity at the  $\alpha$ -position of the unsubstituted five-membered heterocyclic ring in **22**, **25**, and **26** to react with 2-methylthio-1,3-dithiolium methyl sulfate (**12a**) or (**12b**). This result is in sharp contrast to unsuccessful synthesis of the biphenoquinoid compound by the Gompper reaction between 4-dicyanomethylbiphenyl and **12a**.<sup>7</sup>



**Scheme 4.** Synthesis of push-pull heteroquinoid compounds (**8–10**).

All the heteroquinoid compounds (**4–10**) were fully characterized by spectroscopic and elemental analyses. The simple heteroquinoid compounds (**4a**, **6a**, and **7a**) are reasonably soluble in common solvents, and their hexyl- and/or octylthio derivatives are much more soluble. In contrast, the extended compounds (**8a**, **9a**, and **10a**) are too insoluble to permit their NMR measurements; for example, the solubility of **8a** ( $<10^{-5}$  mol/L in chloroform) is reduced by more than two orders in magnitude as compared to that ( $3 \times 10^{-3}$  mol/L) of **4a**. However, the octylthio derivatives (**8b** and **9b**) have solubilities enough to give their proton NMR spectra.

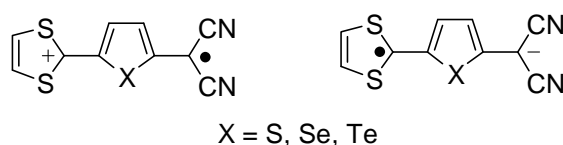
**Redox potentials.** The present push-pull heteroquinoid compounds (**4–10**) like the benzoquinoid counterpart (**1**) are expected to behave as amphoteric redox systems. In fact, their cyclic voltammograms showed an oxidation wave on the anodic region and a reduction wave on the cathodic region. Figure 1 represents the cyclic voltammograms of the thienoquinoid (**4a**) and the bithienoquinoid (**9a**). The oxidation wave forming a radical cation is reversible, whereas the reduction wave forming a radical anion is irreversible. Figure 1 also shows that the quinoid extension from **4a** to **9a** leads to a marked decrease in the potential difference between the oxidation and reduction waves, that is, incremental amphotericity (*vide infra*).



**Figure 1.** Cyclic voltammograms of thienoquinoid (**4a**) and bithienoquinoid (**9a**) in benzonitrile.

The oxidation and reduction potentials of all the push-pull compounds (**4–10**) are compared in Table 1. In comparison of three heteroquinoid compounds (**4a**, **6a**, and **7a**), their oxidation potentials and the reduction potentials are situated in the narrow ranges of +1.00 to +1.03 V and of  $-0.89$  to  $-0.95$  V, respectively. Apparently the electronic effects of the different heteroatoms, that is, sulfur, selenium, and tellurium, incorporated in the heteroquinoid rings have little influence on the electrochemical characters of these compounds. In addition, the octylthio substituents of the derivatives (**4b**, **6b**, and **7b**) have essentially little influence on the oxidation potentials. However, the hexyl substituent on the

thienoquinoid frameworks of **5a** and **5b** tends to somewhat lower both oxidation and reduction potentials. When compared to those ( $E^{\text{ox}}$  +0.79 V and  $E^{\text{red}}$  -0.85 V) of the benzoquinoid compound (**1**), the oxidation potentials of the heteroquinoid compounds (**4a**, **6a**, and **7a**) are much higher, and the reduction potentials are much lower. Evidently, amphotericity is much reduced for these heteroquinoid systems. This means that, owing to the decreasing aromaticity of heteroaromatics relative to benzene, the oxidation and reduction states of these compounds shown in Figure 2 can not stabilize so largely as those of **1**. On the other hand, the thienothienoquinoid compounds show nearly the same oxidation (**8a**, +0.78 V and **8b**, +0.77 V) and reduction potentials (**8a**, -0.78 V and **8b**, -0.79 V) as **1**. Furthermore, the oxidation potentials and reduction potentials of the bithienoquinoid (**9a,b**) and the biselenoquinoid (**10a**) are shifted to the ranges of +0.58 to +0.61 V and of -0.60 to -0.65 V, respectively. Evidently, the increasing heterocyclic rings in the central heteroquinoid skeleton cause marked stabilization for the oxidation and reduction states.



**Figure 2.** Molecular structures of **4a**, **6a**, and **7a** in the oxidation state (left) and the reduction state (right).

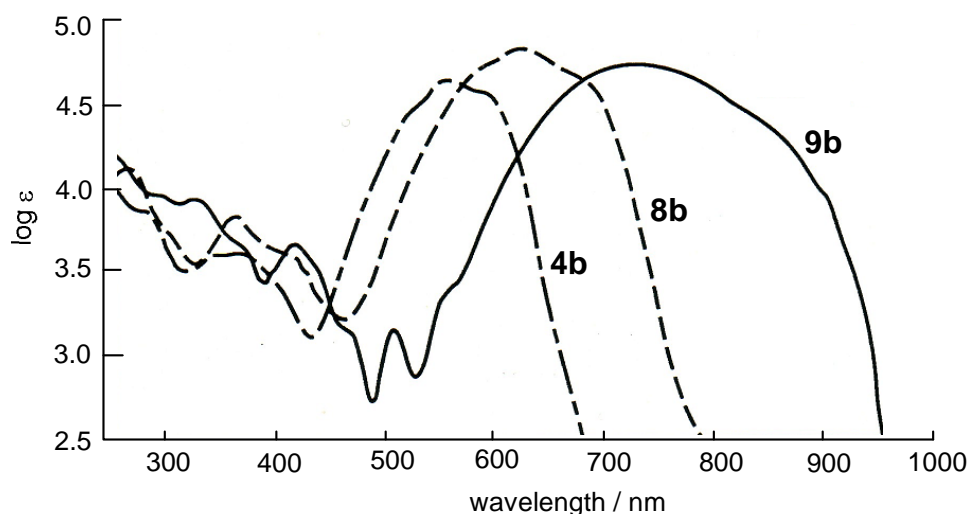
**Table 1.** Redox potentials, electronic absorption maxima, and nitrile vibrational frequencies of push-pull heteroquinoid compounds

Compd	Appearance	$E^{\text{ox}}/\text{V}^{\text{a}}$	$E^{\text{red}}/\text{V}^{\text{a}}$	$E^{\text{ox}}-E^{\text{red}}/\text{V}$	$\lambda_{\text{max}}/\text{nm}$ ( $\log \epsilon$ ) <sup>b</sup>	$\nu_{\text{CN}}/\text{cm}^{-1}$ <sup>c</sup>
<b>4a</b>	blue needle	+1.00	-0.95	1.95	549 (4.68), 588 (4.59)	2199
<b>4b</b>	golden	+1.00	-0.98	1.98	552 (4.65)	2201
<b>5a</b>	purple	+0.95	-1.00	1.95	553 (4.70)	2204
<b>5b</b>	purple	+0.94	-1.01	1.95	553 (4.70)	2201
<b>6a</b>	blue needle	+1.03	-0.95	1.98	548 (4.67), 584 (4.60)	2203
<b>6b</b>	purple needle	+1.01	-0.98	1.99	551 (4.62)	2205
<b>7a</b>	dark green needle	+1.00	-0.89	1.89	553 (4.58), 586 (4.71)	2199
<b>7b</b>	dark green needle	+1.01	-0.98	1.99	561 (4.61)	2203
<b>8a</b>	purple powder	+0.78	-0.78	1.56	625 (4.70), 679 (4.56)	2197
<b>8b</b>	dark green powder	+0.77	-0.79	1.56	622 (4.84)	2201
<b>9a</b>	golden needle	+0.58	-0.60	1.18	739 (4.36)	2191
<b>9b</b>	dark blue powder	+0.61	-0.65	1.26	706 (4.74)	2197
<b>10a</b>	golden powder	+0.59	-0.64	1.23	710 (4.74)	2195

<sup>a</sup>RE, Ag/AgCl; WE, Pt; solvent, PhCN; SE, Bu<sub>4</sub>NClO<sub>4</sub>; scan rate, 100 mV s<sup>-1</sup>. <sup>b</sup>Measured in THF.

<sup>c</sup>Measured on a KBr pellet.

**Electronic spectra.** Owing to reduced HOMO-LUMO gaps due to high amphotericity, all the push-pull heteroquinoid compounds (**4–10**) are highly colored, and their appearances in solid phases are indicated in Table 1. The colors of these compounds are ascribable to a strong intramolecular charge-transfer (CT) electronic transition in the visible region. Figure 3 shows the electronic spectra of three heteroquinoid systems (**4b**, **8b**, and **9b**) in tetrahydrofuran, which represent spectral features of the color-determining CT bands of the respective heteroquinoid systems, and Table 1 also summarizes the CT absorption maxima of all the heteroquinoid chromophores. The absorption maxima of the simple heteroquinoid compounds (**4–7**) appear in the region of 540–600 nm, and the CT bands are little influenced by the kinds of the heteroatoms and the hexyl and/or octylthio substituents. On the other hand, the absorption maxima of the extended thienothienoquinoid compounds (**8a,b**) appear at ca. 650 nm. Furthermore, in accord with high amphotericity, the absorption maxima of the more extended bithienoquinoid (**9a,b**) and biselenoquinoid (**10a**) are markedly shifted to ca. 750 nm, and the absorption edges extend to the near-infrared region around 950 nm.



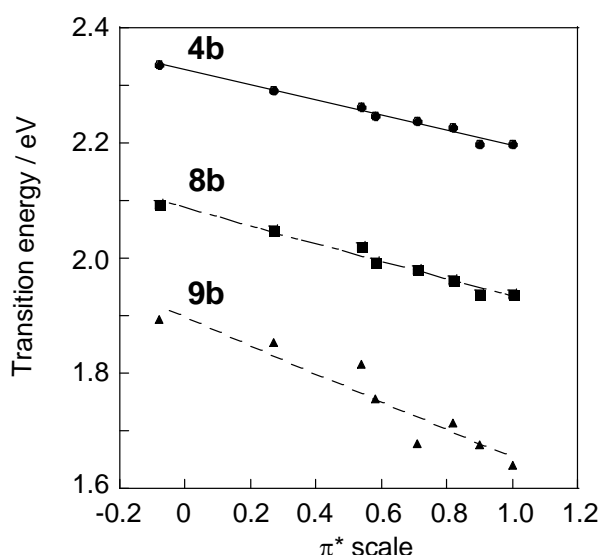
**Figure 3.** The electronic absorption spectra of three heteroquinoid compounds (**4b**, **8b**, and **9b**) in THF.

As expected from CT transitions, the absorption bands of all heteroquinoid compounds demonstrate large solvent dependency. The wavelengths of well-defined peaks (mostly the most intensive peaks) evaluated in various solvents for highly soluble compounds (**4b**, **6b**, **7b**, **8b**, and **9b**) are summarized in Table 2. The solvatochromisms of all compounds are positive. That is, the CT bands of the simple heteroquinoid compounds (**4b**, **6b**, and **7b**) are red-shifted by ca. 30 nm in going from non-polar hexane to highly polar DMSO. Furthermore, the CT bands of the extended heteroquinoid compounds (**8b** and **9b**) are more largely red-shifted by 48 nm and 101 nm, respectively. Figure 4 demonstrates good correlations of the CT transition energies of **4b**, **8b**, and **9b** with  $\pi^*$  scales of solvent polarity defined by Taft *et al.*<sup>16</sup> The same correlations are also observed for **6b** and **7b**.

**Table 2.** CT absorption bands ( $\lambda_{\max}/\text{nm}$ )<sup>a</sup> of soluble heteroquinoid compounds in various solvents

Compd	hexane	ether	toluene	THF	acetone	CH <sub>2</sub> CH <sub>2</sub>	PhCN	DMSO
$\pi^*$ scale <sup>b</sup>	-0.08	0.27	0.54	0.58	0.71	0.82	0.90	1.00
<b>4b</b>	531	541	548	552	554	557	564	564
<b>6b</b>	529	539	547	551	555	557	565	564
<b>7b</b>	532	548	555	561	561	560	570	570
<b>8b</b>	592	605	614	622	626	632	640	640
<b>9b</b>	655	669	683	706	739	724	740	756

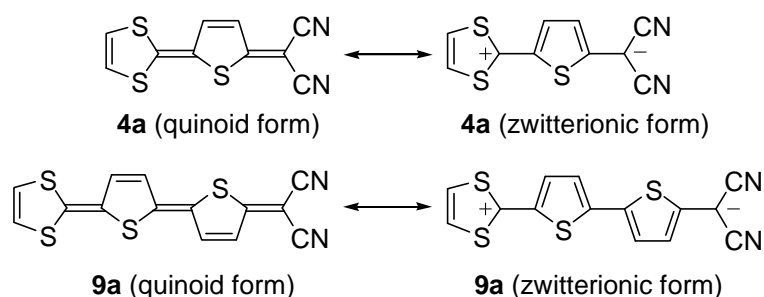
<sup>a</sup>As the CT bands are often structured, only the most intense peaks are compared. <sup>b</sup>Reference 16.

**Figure 4.** Solvent dependency of the CT absorption bands of **4b**, **8b**, and **9b** with  $\pi^*$  scales.

The solvent dependency with  $\pi^*$  scales means that, although they assume considerably polarizable characters, the push-pull heteroquinoid compounds still prefer the neutral ground states. The increasing solvent dependency in the order of **4b**, **8b**, and **9b** indicates more polarizable structures for the extended heteroquinoid systems.

**Hybrid structures.** As represented for **4a** and **9a** in Figure 5, the push-pull quinoid compounds (**4–10**) can exist as a resonance hybrid between the quinoid form and the zwitterionic form, and accordingly, assume highly polarizable characters in nature. This hybridization is induced not only by charge stabilization due to the push-pull electronic effects of both terminal donor and acceptor groups but also by aromatization of the central heteroquinoid ring in the zwitterionic form. The extent of the resonance hybridization can be conveniently evaluated by measuring the nitrile vibrational frequency.<sup>17</sup> Thus, the increasing contribution of the zwitterionic form to the resonance structure causes a low-wavenumber shift for the nitrile vibrational frequency. Table 1 also summarizes the nitrile vibrational frequencies of a

series of the push-pull quinoid compounds (**4–10**). The vibrational frequency ( $2199\text{ cm}^{-1}$ ) of the thienoquinoid compound (**4a**) is much lower than that ( $2227\text{ cm}^{-1}$ ) of thiophene-TCNQ (**3**,  $X = S$ )<sup>9</sup> as a thienoquinoid standard, supporting the considerable contribution of the zwitterionic form to the resonance structure. Considering that the lithium radical anion salt of thiophene-TCNQ shows a nitrile vibrational frequency of  $2193\text{ cm}^{-1}$ ,<sup>18</sup> a proportional calculation indicates a polarity of 41% for **4a**. The octylthio and hexyl substituents in **4b** and **5a,b** tend to a little increase the nitrile frequencies ( $2201\text{--}2204\text{ cm}^{-1}$ ). The selenoquinoid analogue (**6a**) shows a somewhat increasing frequency ( $2203\text{ cm}^{-1}$ ), while the telluroquinoid analogue (**7a**) shows the same ( $2199\text{ cm}^{-1}$ ) as observed for **4a**. These observations indicate that the simple heteroquinoid compounds (**4–7**) assume essentially the same polarizable hybrid structures. On the other hand, the thienothienoquinoid (**8a**), the bithienoquinoid (**9a**), and the biselenoquinoid (**10a**) demonstrate much lower frequencies  $2197$ ,  $2191$ ,  $2195\text{ cm}^{-1}$ , respectively. The low wavenumber shifts of these extended heteroquinoid systems are compatible with increasing polarizable structures, above-speculated based on solvent dependency. The resonance hybrid structures of the extended heteroquinoid systems is much induced by increasing gain in aromaticity of the heterocyclic rings in the zwitterionic form (see Figure 5).

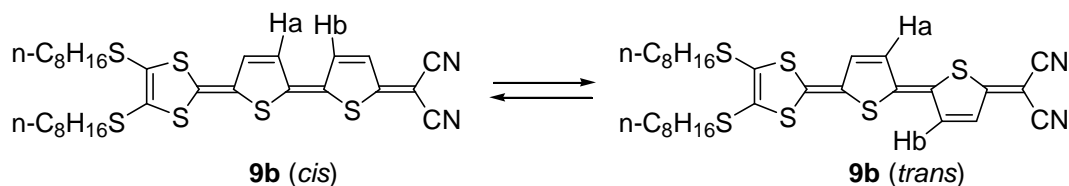


**Figure 5.** Resonance structures of **4a** and **9b**.

It is worth discussing that the molecular structures for **9a,b** and **10a** are comprised of geometrical isomers regarding the central double bond in the biheteroquinoid skeleton, as depicted for **9b** in Figure 6. The <sup>1</sup>H NMR spectrum of **9b** demonstrates two sets of AB signal patterns for the heteroquinoid protons (see the experimental part), indicating that it actually exists in a mixture of the *cis/trans* isomers. The peak integrals indicate that the isomeric population ratio is 1.3:1, and an NOE observation between the adjacent protons Ha and Hb of the *cis* form supports that the major isomer is the *cis* form. A variable temperature NMR measurement in tetrachloroethane-*d*<sub>2</sub> indicates that the respective sets of the *cis* and *trans* signals coalesce at 90 °C. The ready interconversion between the *cis* and *trans* forms at 90 °C is caused by partial mixing of the central double bond with a single-bond character due to resonance hybridization of the quinoid and zwitterionic forms, as above described in the IR analyses. Interestingly enough, the NMR measurement in dimethylsulfoxide-*d*<sub>6</sub> reveals that the coalescence already occurs at

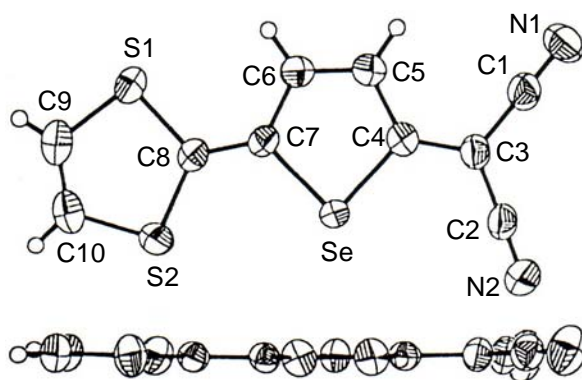


30 °C. It is evident that the increase of solvent polarity enhances the contribution of the zwitterionic form to the resonance hybrid structure, as a result of increasing mixing with a single-bond character resulting in marked lowering of the interconversion barrier. Although no NMR spectra were measured owing to their insolubility, **9a** and **10a** are also considered to be composed of *cis/trans* geometrical isomers.

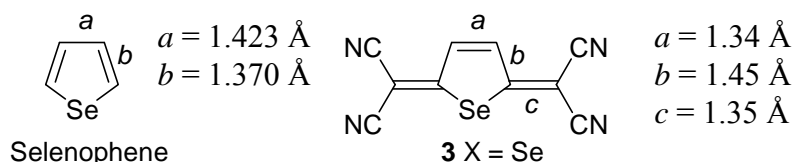


**Figure 6.** Geometrical interconversion of **9b**.

**Crystal structures.** Recrystallization of the selenoquinoid compound (**6a**) from acetone gave a purple needle single crystal, which was examined by X-Ray crystallographic analysis. Figure 7 depicts the molecular structure of **6a**, which is completely planar. When compared to the molecular structures of selenophene<sup>19</sup> and selenophene-TCNQ (**3**, X = Se)<sup>9</sup> (Figure 8), the central heterocyclic ring of **6a** shows the following bond alternation features: the C5–C6 bond (1.334 Å) of **6a** is shorter than the *a*-marked bond (1.423 Å) of selenophene and equal to the *a*-marked bond (1.34 Å) of selenophene-TCNQ. On the other hand, the C4–C5 bond (1.417 Å) and the C6–C7 bond (1.399 Å) are longer than the *b*-marked bond (1.370 Å) of selenophene and shorter than the *b*-marked bond (1.45 Å) of selenophene-TCNQ. In



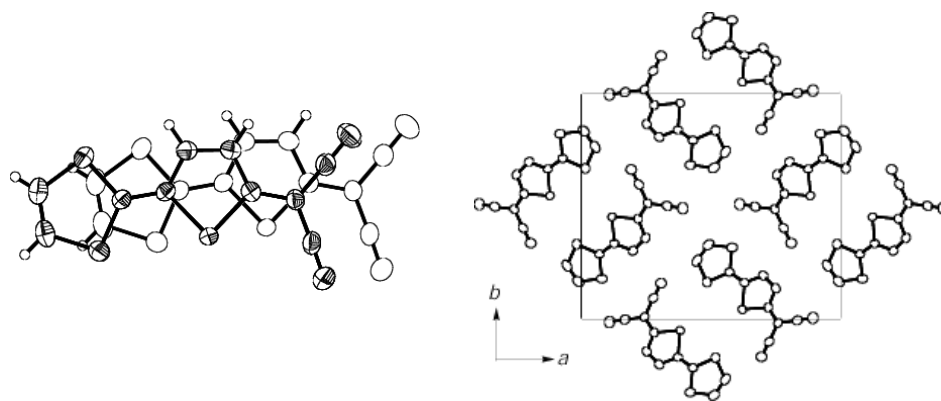
**Figure 7.** Molecular structure of **6a** (top, upper view; bottom, side view) and its bond lengths: C1–N1, 1.134 Å; C2–N2, 1.137 Å; C1–C3, 1.434 Å; C2–C3, 1.411 Å; C3–C4, 1.380 Å; C4–C5, 1.417 Å; C5–C6, 1.334 Å; C6–C7, 1.399 Å; C4–Se, 1.886 Å; C7–Se, 1.909 Å; C7–C8, 1.374 Å; C8–S1, 1.723 Å; C8–S2, 1.725 Å; C9–S1, 1.726 Å; C10–S2, 1.725 Å; C9–C10, 1.316 Å.



**Figure 8.** Selected bond lengths of selenophene and selenophene-TCNQ (**3** X = Se).

addition, the C3–C4 bond (1.380 Å) is longer than the *c*-marked bond (1.35 Å) of selenophene-TCNQ. These features of bond alternations are rationally accommodated by the structural speculation that the selenoquinoid compound (**6a**) exists as a hybrid of the quinoid form and the zwitterionic form, but the central heterocyclic ring still keeps a predominant quinoid framework, as above discussed on the infrared spectroscopy. The thienoquinoid compound (**4a**) has a similar molecular structure,<sup>11</sup> and the theoretical calculation of **4a** at the B3LYP/6-31G\*\* level is in good agreement with the X-Ray structure with the predominant quinoid framework, though there is a certain resonance contribution from the zwitterionic structure.<sup>20</sup>

The crystal structure is characterized by stacking columns of the molecules along the *c*-axis direction (Figure 9). The ring-over-bond sliding stack of the molecules with the same heading is very unusual for the stacking mode of push-pull polarizable molecules. The interplanar distance is 3.52 Å, indicating van der Waals contacts of the  $\pi$ -conjugated system. It is worthy of note that two neighboring molecule in the lateral direction are arranged with an antiparallel alignment to each other. Close heteroatomic distances between the neighboring molecules are 3.35 Å for S---N and 4.61 Å for S---Se. The neighboring couple are surrounded with other molecular couples from all quarters. It can be thus understood that in the crystal, the polarizable character of the molecule is canceled by a dipole interaction with the neighboring molecule in the lateral direction but not with the stacked molecule.



**Figure 9.** Crystal structures of **6a**: left, overlapping view and right, upper view along the *c*-axis.

**Conclusion.** We have synthesized a variety of push-pull heteroquinoid compounds (**4–10**) bearing a strongly electron-donating 1,3-dithiol-2-ylidene group and a strongly electron-accepting dicyanomethylene group. It has turned out that these compounds show high amphotericity in the electrochemical reactions and assume deep colors owing to a strong CT absorption band in the visible region. They exist as a resonance hybrid between the predominant quinoid form and the zwitterionic form, which is induced not only by charge stabilization due to the push-pull electronic effects of the terminal donor and acceptor groups but also by aromaticity gain of the heterocyclic rings in the zwitterionic form. In particular, the extensively conjugated biheteroquinoid compounds (**9a,b** and **10a**)

demonstrate highly polarizable characters. Besides high amphotericity, deep coloration, and high polarizability, the present push-pull heteroquinoid compounds are expected to show further intriguing optoelectronic properties. As observed for push-pull benzoquinoid systems (diamino-substituted dicyanoquinodimethanes),<sup>21,22</sup> Wada and Sasabe actually revealed that when measured in chloroform by the Hyper-Rayleigh Scattering method, compounds (**5b** and **9b**) demonstrated second-order hyperpolarizabilities,  $\beta$   $1300 \times 10^{-30}$  esu and  $2400 \times 10^{-30}$  esu, respectively, which were extraordinarily higher than the value ( $29 \times 10^{-30}$  esu) of standard *p*-nitroaniline.<sup>23</sup>

## EXPERIMENTAL

All chemicals and solvents are of reagent grade. All reactions were carried out under a nitrogen atmosphere. Melting points are uncorrected. Nuclear magnetic resonance spectra were measured in deuteriochloroform at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C with TMS as internal reference, unless otherwise noted. Mass spectral data were obtained using an electron impact ionization procedure (70 eV), unless otherwise noted. The molecular ion peaks of the selenium- and tellurium-containing compounds showed typical isotropic patterns of Se and Te. 1,3-Dithiole-2-thione (**11a**) is commercially available.

**4,5-Bis(octylthio)-1,3-dithiole-2-thione (11b).** 1-Octylbromide (1.23 g, 6.36 mmol) was added to commercially available bis(tetrabutylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolato) zinc complex (1.5 g, 1.59 mmol) dissolved in acetone (20 mL). The mixture was refluxed for 5 h. After the solvent was concentrated, the residual material was dissolved with dichloromethane (50 mL) and the organic layer was washed with water (30 mL), dried, and concentrated. The crude material was purified by column-chromatography on silica gel (hexane) to give **11b** as a yellow oil (1.32 g, 93% yield): IR (neat) 1068 (C=S)  $\text{cm}^{-1}$ ; MS *m/z* 422 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{19}\text{H}_{34}\text{S}_5$ : C, 53.98; H, 8.11. Found: C, 53.81; H, 8.09.

**2-(Dicyanomethyl)chalcogenophenes (17–20), 2-(dicyanomethyl)thieno[3,2-*b*]thiophene (22), and 5-(dicyanomethyl)-2,2'-bichalcogenophenes (25 and 26).** All the 2-dicyanomethylchalcogenophenes were readily obtained by the Takahashi synthetic method that was originally developed for the formation of dicyanomethylbenzene by a substitution reaction between sodium dicyanomethanide and iodobenzene in the presence of a Pd(0) catalyst.<sup>13</sup> The syntheses of **17**, **19**, **20**, and **22** using this method were already reported by Takahashi and Tarutani.<sup>14</sup> A typical procedure is described for the preparation of 2-dicyanomethylthiophene (**17**) as follows. Under a nitrogen atmosphere, malononitrile (670 mg, 10 mmol) was added to a suspension of 60% oily sodium hydride (800 mg, 20 mmol) in dry THF (50 mL), and the mixture was stirred for 1 h. After 2-iodothiophene (**13**)<sup>24</sup> (2.1 g, 10 mmol) and tetrakis(triphenylphosphine)palladium (1.5 g, 1.3 mmol) were added, the mixture was refluxed for 3 h.

Ice (20 g) and water (20 mL) were successively added with ice-cooling to quench the reaction, and then the solution was concentrated in vacuo to remove most of the THF. The resulting aqueous solution was acidified with 1 *N* hydrochloric acid to pH 3–4 and then extracted with dichloromethane (100 mL). The organic phase was separated, washed with brine, and dried (MgSO<sub>4</sub>). After evaporation of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane as eluent to give a red oil of **17** (530 mg, 55% yield): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.19 (dt, *J* = 6.0, 2.9 Hz, 1H), 7.06 (dt, *J* = 6.0, 1.9 Hz, 1H), 4.41 (dd, *J* = 2.9, 1.9 Hz, 2H); MS *m/z* 148 (M<sup>+</sup>); Anal. Calcd for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>S: C, 56.75; H, 2.70; N, 18.92. Found: C, 56.73; H, 2.70; N, 18.88.

**2-(Dicyanomethyl)-3-hexylthiophene (18)**: 30% yield from 2-iodo-3-hexylthiophene (**14**);<sup>25</sup> a red oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.30 (d, *J* = 5.1 Hz, 1H), 6.90 (d, *J* = 5.1 Hz, 1H), 5.20 (s, 1H), 2.63 (t, *J* = 7.0 Hz, 2H), 0.7–1.9 (m, 11H); Anal. Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>S: C, 67.20; H, 6.94; N, 12.06. Found: C, 67.25; H, 6.91; N, 12.00.

**2-(Dicyanomethyl)selenophene (19)**: 64% yield from 2-iodoselenophene (**15**); colorless crystals from chloroform–hexane; mp 124–125 °C dec. (lit.,<sup>14</sup> mp 119–123 °C dec.); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0–7.2 (m, 2H), 4.52 (d, *J* = 0.8 Hz, 2H); MS *m/z* 196 (M<sup>+</sup>); Anal. Calcd for C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>Se: C, 43.10; H, 2.07; N, 14.36. Found: C, 43.10; H, 2.06; N, 14.36.

**2-(Dicyanomethyl)tellurophene (20)**: 35% yield from 2-iodotellurophene (**16**); pale yellow crystals from chloroform–hexane; mp 118–121 °C (lit.,<sup>14</sup> mp 99–101 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.23 (dt, *J* = 6.3, 2.8 Hz, 1H), 7.12 (dt, *J* = 6.3, 1.8 Hz, 1H), 4.56 (dd, *J* = 2.8, 1.8 Hz, 2H); MS *m/z* 246 (M<sup>+</sup> based on <sup>130</sup>Te).

**2-(Dicyanomethyl)thieno[3,2-*b*]thiophene (22)**: 53% yield from 2-iodothieno[3,2-*b*]thiophene (**21**); pale red crystals from chloroform; mp 142–143 °C (lit.,<sup>14</sup> 138–139 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.53 (d, *J* = 5.3 Hz, 1H); 7.29 (d, *J* = 5.3 Hz, 1H), 5.34 (s, 1H); MS *m/z* 204 (M<sup>+</sup>).

**5-(Dicyanomethyl)-2,2'-bithiophene (25)**: 43% yield from 5-iodo-2,2'-bithiophene (**23**);<sup>26</sup> colorless plates from chloroform/hexane; mp 125.7–126.3 °C dec.; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.00–7.30 (m, 5 H), 5.21 (d, *J* = 0.6 Hz, 1H); Anal. Calcd for C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>S<sub>2</sub>: C, 57.37; H, 2.63; N, 12.16. Found: C, 57.34; H, 2.63; N, 12.16.

**5-(Dicyanomethyl)-2,2'-biselenophene (26)**: 26% yield from 5-bromo-2,2'-biselenophene (**24**) prepared by one equimolar bromination of 2,2'-biselenophene with NBS;<sup>27</sup> pale red plates from chloroform; mp 138–139 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.98 (dd, *J* = 5.4, 1.1 Hz, 1H), 7.36 (dd, *J* = 4.0, 1.1 Hz, 1H), 7.29 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.26 (dd, *J* = 5.4, 3.7 Hz, 1H), 7.14 (d, *J* = 4.0 Hz, 1H), 5.29 (d, *J* = 1.1 Hz, 1H); Anal. Calcd for C<sub>30</sub>H<sub>38</sub>N<sub>2</sub>S<sub>4</sub>Se<sub>2</sub>: C, 40.76; H, 1.87; N, 8.64. Found: C, 40.75; H, 1.86; N, 8.48.

**Heteroquinoid Compounds (4–10).** A general procedure is described for the preparation of 2-(dicyanomethylene)-5-(1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (**4a**) as follows. A mixture of commercially available 1,3-dithiole-2-thione (**11a**) (134 mg, 1.0 mmol) and dimethyl sulfate (126 mg, 1.0

mmol) was stirred at 90 °C for 30 min to produce 2-methylthio-1,3-dithiolium methyl sulfate (**12a**). Into the reaction solution were successively added 2-(dicyanomethyl)thiophene (**17**) (150 mg, 1.0 mmol), acetic acid (10 mL), and triethylamine (100 mg), and the mixture was stirred at 110 °C for an hour. After the reaction mixture was cooled, purple solid was filtered and purified by recrystallization from acetone to give **4a** (220 mg, 90% yield) as purple needles: mp >300 °C; <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 7.76 (d, *J* = 5.4 Hz, 1H), 7.46 (d, *J* = 6.4 Hz, 1H), 7.35 (d, *J* = 6.4 Hz, 1H), 6.91 (d, *J* = 5.4 Hz, 1H); MS *m/z* 248 (M<sup>+</sup>); Anal. Calcd for C<sub>10</sub>H<sub>4</sub>S<sub>3</sub>N<sub>2</sub>: C, 48.37; H, 1.62; N, 11.28. Found: C, 48.17; H, 1.61; N, 11.23.

**2-(Dicyanomethylene)-5-[4,5-bis(octylthio)-1,3-dithiol-2-ylidene]-2,5-dihydrothiophene (4b)**: 42% yield from **12b**, *in situ* generated from **11b**, and **17**; golden crystals from acetic acid; mp 95–96 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.20 (d, *J* = 5.4 Hz, 1H), 6.92 (d, *J* = 5.4 Hz, 1H), 2.89 (m, 4H), 1.67 (m, 4H), 1.43 (m, 4H), 1.29 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 172.4, 148.5, 138.1, 131.8, 131.6, 125.7, 123.0, 115.5, 114.7, 60.2, 36.9, 31.8, 29.7, 29.1, 29.0, 28.5, 22.6, 14.1; MS *m/z* 536 (M<sup>+</sup>); Calcd for C<sub>26</sub>H<sub>36</sub>S<sub>5</sub>N<sub>2</sub>: C, 58.20; H, 6.72; N, 5.22. Found: C, 58.13; H, 6.66; N, 5.12.

**2-(Dicyanomethylene)-5-(1,3-dithiol-2-ylidene)-3-hexyl-2,5-dihydrothiophene (5a)**: 80% yield from **12a** and **18**; purple needles from hexane; mp 173–174 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.97 (s, 1H), 6.82 (d, *J* = 6.5 Hz, 1H), 6.79 (d, *J* = 6.5 Hz, 1H), 2.74 (t, *J* = 7.7 Hz, 2H), 1.61 (m, 2H), 1.41 (m, 2H), 1.33 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>S<sub>3</sub>: C, 57.80; H, 4.85; N, 8.42. Found: C, 57.80; H, 4.85; N, 8.36.

**2-(Dicyanomethyl)-5-[4,5-bis(octylthio)-1,3-dithiol-2-ylidene]-3-hexyl-2,5-dihydrothiophene (5b)**: 38% yield from **12b** and **18**; purple needles from hexane; mp 72–73 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 6.90 (s, 1H), 2.88 (m, 4H), 2.74 (t, *J* = 7.8 Hz, 2H), 1.66 (m, 4H), 1.60 (m, 2H), 1.25–1.35 (m, 20H), 0.89 (m, 9H); Anal. Calcd for C<sub>32</sub>H<sub>48</sub>N<sub>2</sub>S<sub>5</sub>: C, 61.64; H, 7.74; N, 4.52. Found: C, 61.90; H, 7.61; N, 4.50.

**2-(Dicyanomethylene)-5-(1,3-dithiol-2-ylidene)-2,5-dihydroselephenone (6a)**: 95% yield from **12a** and **19**; purple needles from acetone; mp >300 °C; <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 7.76 (d, *J* = 5.4 Hz, 1H), 7.46 (d, *J* = 6.4 Hz, 1H), 7.35 (d, *J* = 6.4 Hz, 1H), 6.91 (d, *J* = 5.4 Hz, 1H); MS *m/z* 296 (M<sup>+</sup>, <sup>80</sup>Se); Calcd for C<sub>10</sub>H<sub>4</sub>N<sub>2</sub>S<sub>2</sub>Se: C, 40.68; H, 1.37; N, 9.49. Found: C, 40.60; H, 1.31; N, 9.44.

**2-(Dicyanomethylene)-5-[4,5-bis(octylthio)-1,3-dithiol-2-ylidene]-2,5-dihydroselephenone (6b)**: 36% yield from **12b** and **19**; purple needles from hexane; mp 83–84 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.25 (d, *J* = 5.6 Hz, 1H), 6.92 (d, *J* = 5.6 Hz, 1H), 2.89 (t, *J* = 7.4 Hz, 4H), 1.66 (quin, *J* = 7.4 Hz, 4H), 1.42 (m, 4H), 1.29 (m, 16H), 0.89 (t, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 176.9, 150.0, 140.9, 132.0, 130.9, 126.6, 122.1, 116.3, 114.4, 36.8, 31.8, 29.7, 29.1, 29.0, 28.4, 22.6, 14.1; MS *m/z* 584 (M<sup>+</sup>, <sup>80</sup>Se); Anal. Calcd for C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>S<sub>4</sub>Se: C, 53.49; H, 6.21; N, 4.79. Found: C, 53.32; H, 6.11; N, 4.79.

**2-(Dicyanomethylene)-5-(1,3-dithiol-2-ylidene)-2,5-dihydrotellurophene (7a)**: 95% yield from **12a** and **20**; purple needles from acetone; mp >300 °C; <sup>1</sup>H NMR (acetone-d<sub>6</sub>) δ 7.76 (d, *J* = 5.4 Hz, 1H), 7.46

(d,  $J = 6.4$  Hz, 1H), 7.35 (d,  $J = 6.4$  Hz, 1H), 6.91 (d,  $J = 5.4$  Hz, 1H); MS  $m/z$  344 ( $M^+$ ,  $^{128}\text{Te}$ ); Anal. Calcd for  $\text{C}_{10}\text{H}_4\text{N}_2\text{S}_2\text{Te}$ : C, 34.93; H, 1.17; N, 8.15. Found: C, 34.88; H, 1.07; N, 8.02.

**2-(Dicyanomethylene)-5-[4,5-bis(octylthio)-1,3-dithiol-2-ylidene]-2,5-dihydrotellurophene (7b)**: 45% yield from **12b** and **20**; dark green needles from hexane; mp 115–116 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.30 (d,  $J = 6.2$  Hz, 1H), 6.95 (d,  $J = 6.2$  Hz, 1H), 2.88 (m, 4 H), 1.66 (m, 4H), 1.42 (m, 4H), 1.28 (m, 16H), 0.89 (t,  $J = 6.7$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  172.7, 154.9, 132.3, 130.6, 130.0, 117.7, 114.3, 110.9, 92.4, 73.2, 36.8, 36.7, 31.8, 29.7, 29.6, 29.1, 29.0, 28.48, 28.46, 22.6; MS  $m/z$  634 ( $M^+$ ,  $^{128}\text{Te}$ ); Anal. Calcd for  $\text{C}_{26}\text{H}_{36}\text{N}_2\text{S}_4\text{Te}$ : C, 49.37; H, 5.73; N, 4.42. Found: C, 49.35; H, 5.71; N, 4.37.

**2-(Dicyanomethylene)-5-(1,3-dithiol-2-ylidene)-2,5-dihydrothieno[3,2-*b*]thiophene (8a)**: 83% yield from **12a** and **22**; a purple powder from acetone; mp >300 °C; MS  $m/z$  304 ( $M^+$  based on  $^{130}\text{Te}$ ); Anal. Calcd for  $\text{C}_{12}\text{H}_4\text{N}_2\text{S}_4$ : C, 47.35; H, 1.32; N, 9.20. Found: C, 47.33; H, 1.32; N, 9.20.

**2-(Dicyanomethylene)-5-[4,5-bis(octylthio)-1,3-dithiol-2-ylidene]-2,5-dihydrothieno[3,2-*b*]thiophene (8b)**: 54% yield from **12b** and **22**; a dark green powder from benzene; mp 238–239 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.99 (d,  $J = 0.9$  Hz, 1H), 6.81 (d,  $J = 0.9$  Hz, 1H), 2.89 (m, 4H), 1.67 (m, 4H), 1.56 (m, 4H), 1.29 (m, 16H), 0.88 (t,  $J = 6.8$  Hz, 6H); MS  $m/z$  592 ( $M^+$ ); Anal. Calcd for  $\text{C}_{28}\text{H}_{36}\text{N}_2\text{S}_6$ : C, 56.72; H, 6.12; N, 4.72. Found: C, 56.72; H, 6.02; N, 4.70.

**2-(Dicyanomethylene)-5'-(1,3-dithiol-2-ylidene)-5,5'-dihydro- $\Delta^{2,2'}$ -bithiophene (9a)**: 69% yield from **12a** and **25**; golden needles after sublimation (250 °C/ 1 Torr); mp >300 °C; MS  $m/z$  330 ( $M^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_6\text{N}_2\text{S}_4$ : C, 50.89; H, 1.83; N, 8.48. Found: C, 50.88; H, 1.83; N, 8.47.

**2-(Dicyanomethylene)-5'-[4,5-bis(octylthio)-1,3-dithiol-2-ylidene]-5,5'-dihydro- $\Delta^{2,2'}$ -bithiophene (9b)**: 24% yield from **12b** and **25**; dark blue powder from acetic acid; mp 139–140 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) *cis* (aromatic)  $\delta$  7.45 (d,  $J = 5.1$  Hz, 0.57H), 7.05 (d,  $J = 5.5$  Hz, 0.57H), 6.99 (d,  $J = 5.5$  Hz, 0.57H), 6.94 (d,  $J = 5.1$  Hz, 0.57H), *trans* (aromatic)  $\delta$  7.33 (d,  $J = 5.1$  Hz, 0.43H), 7.08 (d,  $J = 5.4$  Hz, 0.43H), 7.03 (d,  $J = 5.1$  Hz, 0.43H), 6.75 (d,  $J = 5.4$  Hz, 0.43H), *cis* and *trans* (alkyl)  $\delta$  2.89 (m, 4H), 1.67 (m, 4H), 1.43 (m, 20H), 0.88 (t,  $J = 6.8$  Hz, 6H); MS  $m/z$  618 ( $M^+$ ); Anal. Calcd for  $\text{C}_{30}\text{H}_{38}\text{N}_2\text{S}_6$ : C, 58.20; H, 6.15; N, 4.53. Found: C, 58.19; H, 6.15; N, 4.48.

**2-(Dicyanomethylene)-5'-(1,3-dithiol-2-ylidene)-5,5'-dihydro- $\Delta^{2,2'}$ -biselenophene (10a)**: 75% yield from **12a** and **26**; a golden powder after sublimation (250 °C/ 1 Torr); mp >300 °C; MS  $m/z$  426 ( $M^+$ ,  $^{80}\text{Se}$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_6\text{N}_2\text{S}_2\text{Se}_2$ : C, 39.64; H, 1.43; N, 6.60. Found: C, 39.67; H, 1.46; N, 6.50.

**X-Ray Crystallographic Analyses of 6a.** X-Ray diffraction experiments were performed at room temperature on a Rigaku AFC6S diffractometer with graphite-monochromated Cu  $K_\alpha$  radiation ( $\lambda = 1.5418$  Å). The intensity data were measured using the  $\omega$ - $2\theta$  scan technique. The structures were solved by direct methods and refined by full-matrix least-squares techniques with anisotropic temperature factors for the non-hydrogen atoms. Crystal data for **6a**: formula  $\text{C}_{10}\text{H}_4\text{S}_2\text{N}_2\text{Se}$ ; formula wt. 295.23;

crystal system monoclinic; space group  $P2_1/n$ ;  $a = 17.665(2)$  Å;  $b = 15.437(2)$  Å;  $c = 3.9257(4)$  Å;  $\beta = 90.77(1)^\circ$ ;  $V = 1070.4(2)$  Å<sup>3</sup>;  $Z = 4$ ;  $D_c = 1.833$  g cm<sup>-3</sup>; NDTA ( $|F_o| \geq 3.0\sigma(|F_o|)$ ) = 1,438;  $R = 2.4\%$ .

## ACKNOWLEDGEMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan. The authors are greatly obliged to Dr. Tatsuo Wada (The Institute of Physical and Chemical Research) and Prof. Hiroyuki Sasabe (Chitose Institute of Science and Technology) for nonlinear optical properties of **5b** and **9b**.

## REFERENCES AND NOTES

1. R. Gompper and H. -U. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1437.
2. J. Fabian, H. Nakazumi, and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197.
3. P. N. Prasad and B. A. Reinhardt, *Chem. Mater.*, 1990, **2**, 660.
4. S. R. Marder and J. W. Perry, *Adv. Mater.*, 1993, **5**, 804.
5. R. Gompper, H. -U. Wagner, and E. Kutter, *Chem. Ber.*, 1968, **101**, 4123.
6. R. Gompper and H. -U. Wagner, *Tetrahedron Lett.*, **1968**, 165.
7. S. Inoue, Y. Aso, and T. Otsubo, *Chem. Commun.*, **1997**, 1105.
8. K. Takahashi, 'TTF Chemistry,' ed. by J. Yamada and T. Sugimoto, Kodansha-Springer, Tokyo, 2005, Chapter 13, pp. 311–337.
9. S. Gronowitz and B. Uppström, *Acta Chem. Scand. B*, 1974, **28**, 981.
10. (a) F. Ogura, T. Otsubo, and Y. Aso, *Sulfur Reports*, 1992, **11**, 439. (b) F. Ogura, T. Otsubo, and Y. Aso, *Pure Appl. Chem.*, 1993, **65**, 683. (c) F. Ogura and T. Otsubo, 'Handbook of Organic Conductive Molecules and Polymers,' ed. by H. S. Nalwa, John Wiley, Chichester, 1997, Vol. 1, Chapter 4, pp. 229–248.
11. A part of the synthetic results of the present push-pull heteroquinoid chromophores (**4–10**) and the molecular structure of the thienoquinoid (**4a**) were preliminarily reported in the Proceedings of the International Conference on Science and Technology of Synthetic Metals, 1996: S. Inoue, S. Mikami, Y. Aso, T. Otsubo, T. Wada, and H. Sasabe, *Synth. Met.*, 1997, **84**, 395.
12. Modified push-pull quinoidal thiophenes with highly soluble structures were recently reported: T. Takahashi, K. Takimiya, T. Otsubo, and Y. Aso, *Org. Lett.*, 2005, **7**, 4313.
13. M. Uno, K. Seto, and S. Takahashi, *J. Chem. Soc., Chem. Commun.*, **1984**, 932.
14. K. Takahashi and S. Tarutani, *Heterocycles*, 1996, **43**, 1927.
15. R. Gompper and E. Kutter, *Chem. Ber.*, 1965, **98**, 1365.
16. M. J. Kamlet, J. L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.

17. The nitrile vibrational frequency of TCNQ is often used for the simple estimation of the degrees of charge-transfer for its molecular complexes: J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.
18. N. F. Haley, *J. Chem. Soc., Chem. Commun.*, **1979**, 1030.
19. R. D. Brown, F. R. Burden, and P. D. Godfrey, *J. Mol. Spect.*, 1968, **25**, 415.
20. B. Milián, E. Ortí, V. Hernández, J. T. L. Navarrete, and T. Otsubo, *J. Phys. Chem. B*, 2003, **107**, 12175.
21. S. J. Lalama, K. D. Singer, A. F. Garito, and K. N. Desai, *Appl. Phys. Lett.*, 1981, **39**, 940.
22. M. Ravi, D. N. Rao, S. Cohen, I. Agranat, and T. P. Radhakrishnan, *Chem. Mater.*, 1997, **9**, 830.
23. K. Tanaka, T. Wada, H. Sasabe, S. Inoue, Y. Aso, and T. Otsubo, The 72 Annual Meeting of Japan Chemical Society, Abstract II, p. 1257, 1997.
24. R. Rossi, A. Carpita, and A. Lezzi, *Tetrahedron*, 1984, **40**, 2773.
25. A. Iraqi and G. W. Baker, *J. Mater. Chem.*, 1998, **8**, 25.
26. R. F. Curtis and G. T. Phillips, *J. Chem. Soc.*, **1965**, 5134.
27. H. Nakanishi, S. Inoue, and T. Otsubo, *Mol. Cryst. Liq. Cryst.*, 1997, **296**, 335