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Synthesis and Properties of Dihexylbithienoquinonoid Derivatives with Head-to-head, Head-to-tail, and Tail-to-tail Orientations

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2,2′-(Dihexyl-2,2′-bithienylidene-5,5′-diylidene)bis(propanedinitrile)s (dihexylbithienoquinonoid derivatives), in which two 3-hexylthiophene moieties are connected with head-to-tail (HT) and tail-to-tail (TT) orientations, were synthesized. HT bithienoquinonoid was isolated in a single form together with a small amount of its bromo derivative, similarly to the case for the head-to-head (HH) orientational isomer. On the other hand, TT isomer exhibited a peculiar feature in solution, affording an equilibrium mixture of two geometrical isomers. Electronic and electrochemical properties of these bithienoquinonoids were studied and compared with those of HH isomer. The results proved that all these bithienoquinonoid compounds possess highly polarizable and electron-acceptable properties. HH bithienoquinonoid was reduced through one two-electron transfer process, while HT and TT isomers were reduced through two one-electron transfer processes via stable radical anions to the corresponding dianions.

Previously, we reported the synthesis of various series of oligo(3-hexylthiophene) derivatives with head-to-head (HH) orientation and showed that their electronically polarizable properties were enhanced with increases of the number of thiophene rings, the electron-withdrawing ability of substituent on the terminal positions, and the molecular planarity for π-electronic conjugation.[1]

Hexylthienoquinonoids, 2,2′-(3-hexyl-2,5-thiophenediylidene)bis(propanedinitrile) (**1**), 2,2′-(3,3′-dihexyl-2,2′,5,5′-tetrahydro-2,2′-bithienylidene-5,5′-diylidene)bis(propanedinitrile) (**2**), and 5,5′-bis(5-dicyanomethylene-3-hexyl-2,5-dihydro-2-thienylidene)-4,4′-dihexyl-2,2′,5,5′-tetrahydro-2,2′-bithienylidene (**3**), not only possessed the exceptionally large nonlinear hyperpolarizability $\langle \gamma \rangle$ as compared with the other oligothiophene derivatives,[2] but also exhibited the electron-acceptable properties[1] as strong as those of the corresponding benzenoid quinodimethanes (Chart 1). Mononucleic thienoquinonoid **1** and tetranucleic thienoquinonoid **3** were electrochemically reduced to proceed via the radical anion through two one-electron transfer processes to form the corresponding dianions, while dinucleic thienoquinonoid **2** proceed through one two-electron transfer process directly to the dianion. It was also proved that the electron-acceptable property of **2** is much lower than those of **1** and **3**, though thienoquinonoids **1**—**3** exist in regularly extended electronic structures. Moreover, the bithienoquinonoid with no alkyl substituent (R = H of **2**) is well known to have much stronger electron-acceptable properties than **2**.[3] These electrochemical properties of bithienoquinonoid **2** were deduced to arise from the HH orientational mode of two 3-hexylthiophene moieties.

In continuation of our investigation on the electronic properties of orientational isomers of the bithiophene derivatives,[4] bithienoquinonoids with head-to-tail (HT) and tail-to-tail (TT) orientations, 2,2′-(3,4′-dihexyl-2,2′,5,5′-tetrahydro-2,2′-bithienylidene-5,5′-diylidene)bis(propanedinitrile) (**4**) and 2,2′-(4,4′-dihexyl-2,2′,5,5′-tetrahydro-2,2′-bithienylidene-5,5′-diylidene)bis(propanedinitrile) (**5**), were synthesized (Chart 1). In this paper, electronic and electrochemical properties of the title bithienoquinonoids with HH, HT, and TT orientations and of their bromo derivatives will be described, along with a peculiar feature of TT isomer **5**.

Results and Discussion

Synthesis of HT and TT Bithienoquinonoids 4 and 5 and the Bromo Derivative 7 of 4. Precursors for the title bithienoquinonoids are dibromides **16** (Scheme 2) and **19** (Scheme 3) of HT and TT bithiophenes **13** and **14** (Scheme 1), respectively.[1] It was found that, under conditions of the higher reaction temperature and the larger reaction scale, oxidative homo coupling reaction of 2-lithio-3-hexylthiophene (**10**) generated from bromide **9** afforded a mixture of HH bithiophene **12** together with HT bithiophene **13** as a by-product. This indicates that the 2-lithiated species **10** isomerizes to the 5-lithiated isomer **11**, as shown in Scheme 1. It was proved that the ratio of HT to HH bithiophene reaches 1 : 1 above the reaction temperature of −40 °C.[5] It is worthy of note that little amount of TT bithiophene **14** could be found in the reaction mixture, in spite of the possible formation of **14** via homo coupling reaction of 5-lithiated species **11**.

Although separation of HT bithiophene **13** from HH isomer **12** was found difficult by ordinary procedures because of their very similar physical properties, the selective bromination of HT bithiophene **13** with NBS led to the simple separation of these orientational isomers, as shown in Scheme 2.[5,6] The product **15** was easily separable from **12** by column chromatography; it was further transformed in more than 90% yield with NBS to HT dibromide **16** for the correspond-

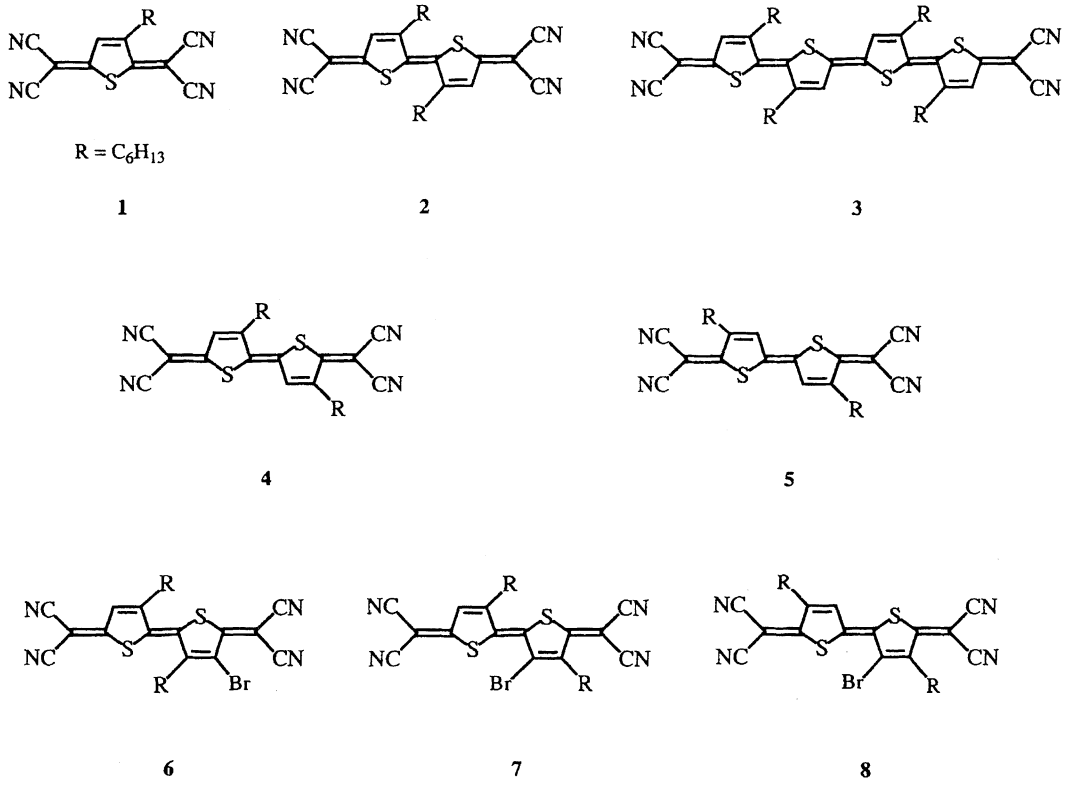
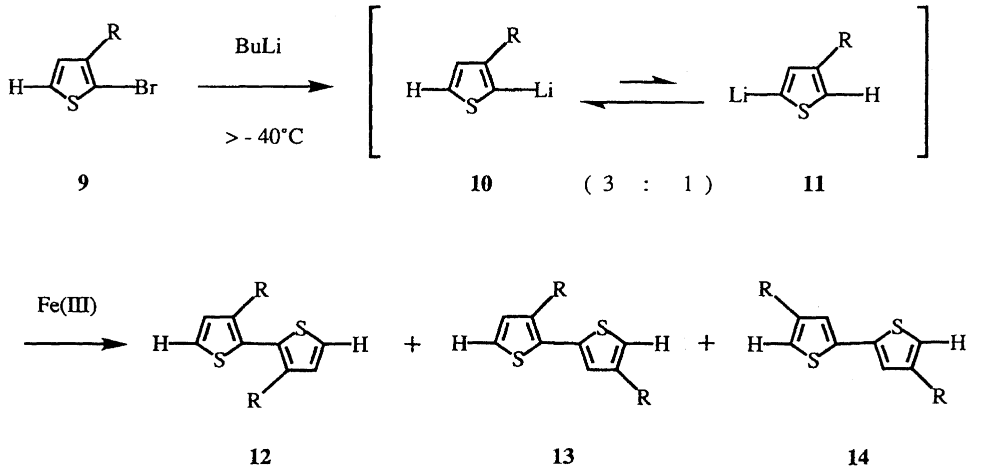
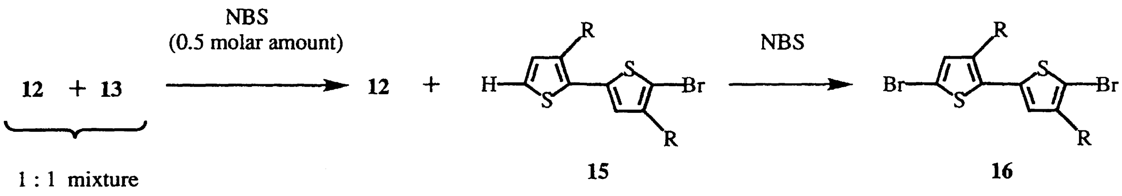


Chart 1.



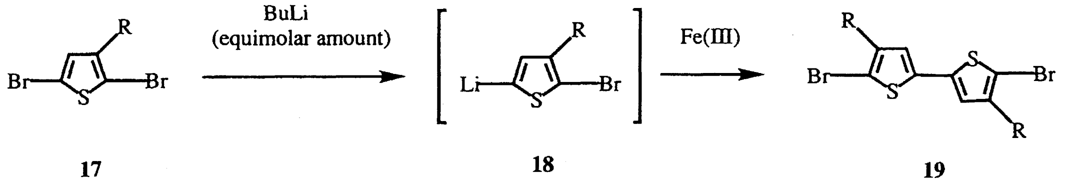
Scheme 1.



Scheme 2.

ing bithienoquinonoid **4**.

TT dibromide **19** for bithienoquinonoid **5** could be directly obtained by homo coupling of 2,5-dibromo-3-hexylthiophene (**17**), as shown in Scheme 3. Thus, lithiation of **17**[1] with one molar amount of butyllithium followed by addition of iron(III) (acetylacetonate)$_3$ (Fe(acac)$_3$)[7] afforded TT bithiophene dibromide **19** as a single product in 55% yield. This result clearly indicates that displacement of the bromo substituent with lithium ion took place exclusively at 5-position of **17** to form **18**. The parent TT bithiophene **14** was also obtained



Scheme 3.

by reduction of **19** with lithium aluminum hydride ($LiAlH_4$) in 93% yield.

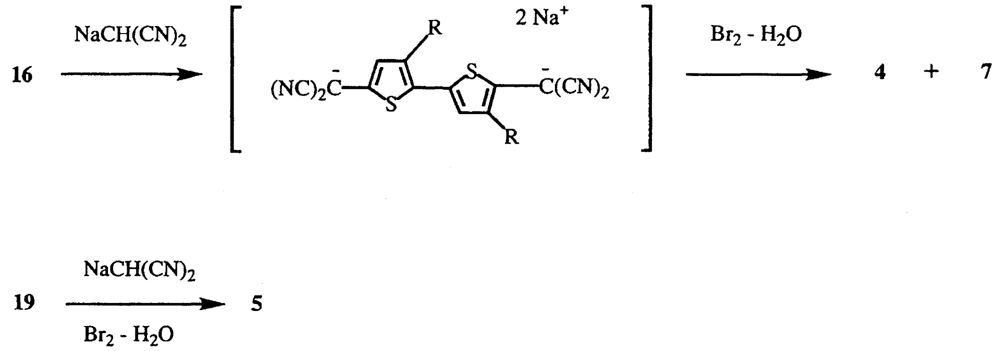
Similarly for HH bithienoquinonoid **2**,[1,3] HT and TT dibromides **16** and **19** thus obtained were treated with sodium dicyanomethanide ($NaCH(CN)_2$) in the presence of tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), followed by oxidation with saturated bromine–water (Br_2–H_2O) to afford the corresponding HT and TT bithienoquinonoids **4** and **5** in 21 and 29% yields, respectively (Scheme 4). Purification of HT and TT bithienoquinonoids **4** and **5** could be achieved by means of column chromatography and recrystallization to afford fully characterizable materials as black purple needles, similarly to that of HH isomer **2**.

Although the reaction mechanism has not been clear, the bromo derivative **7**[8] was obtained as a by-product together with HT bithienoquinonoid **4**, similarly to the case for the bromo derivative **6** together with HH isomer **2**.[1] But the corresponding bromide **8** to TT isomer **5** could not be obtained. Instead, TT isomer **5** in solutions was proved to isomerize to afford an equilibrium mixture between two geometrical species at room temperature, differently from the other HH and HT isomers **2** and **4** (see below).

Structures of bithiophenes and bithienoquinonoids were determined by ^1H NMR spectral measurements, in which **14** reflected C_2 symmetry of TT orientation; the spectra exhibit two singlet signals due to thiophene protons (ThH). It was proved that ThH signals of bithiophenes show the high-field shift in the order of HH (δ = 7.23 and 6.96)[1] < HT (δ = 7.12, 6.94, 6.90, and 6.86)[1] < TT (δ = 6.97 and 6.76) orientations. The same tendency of high-field shift was also observed for ThH signals of bithienoquinonoids; HH (δ = 7.36)[1] < HT (δ = 7.22 and 7.21) < TT (δ = 7.15).

Studies on Electronic Absorption Spectra of Bithienoquinonoids 2, 4, and 5. Maxima and molar extinction coefficients due to the longest wavelength absorption bands for HH, HT, and TT bithienoquinonoids **2**, **4**, and **5** and the corresponding dihexylbithiophenes **12**, **13**, and **14** in dichloromethane (CH_2Cl_2) are summarized in Table 1.

It is well known that 2,2′-bithiophene (**21**; λ = 303 nm, ε = 10600) shows bathochromic shift by ca. 70 nm from thiophene (**20**; λ = 231 nm, ε = 7100) with the molar extinction coefficient reduced from the value ($\varepsilon = 7100\times2$) simply estimated from a dimer of **20**.[1] This result clearly indicates the large π-electronic conjugation between two thiophene rings in **21**. A similar tendency of bathochromic shift to that for **21** was observed for HT bithiophene **13**, of which the absorption maximum is almost comparable to that of **21**. On the other hand, HH bithiophene **12** exhibits the intensive hypsochromic shift by 50 nm from HT isomer **13**, resulting in a small bathochromic shift of 10 nm from 3-hexylthiophene (**22**;[1] λ = 234 nm, ε = 6850). These results can be attributed to the degree of deviation from the molecular planarity for π-electronic conjugation by twisting due to the steric repulsion between hexyl substituent and sulfur atom belonging to the opposite thiophene ring. In the case of dihexylbithiophenes, the respective main bands shifted to the longer wavelengths



Scheme 4.

Table 1. Electronic Absorption Maxima (λ_{max}/nm, (ε) Main Bands in Bold) of Bithienoquinonoids and Bithiophenes in CH_2Cl_2

2	4	5	12	13	14
492 (23500, sh)	500 (38000, sh)	526 (62900, sh)	**247** (16800)	252 (8800)	252 (6400)
519 (48200)	**541** (66100)	**554** (79200)	274 (7400, sh)	**297** (10600)	**311** (9600)
554 (62500)					

in the order of HH ≪ HT < TT orientation with regularly reducing their intensities. The longest wavelength maximum of TT bithiophene **14** exhibited more bathochromic shift by 8 nm from that of the least strained bithiophene **21**, probably in consequence of elevation of HOMO level of bithiophene chromophore due to an inductive effect of hexyl substituent. Thus, it can be concluded that orientation of 3-hexylthiophene ring severely affects the molecular planarity for π-electronic conjugation, i.e., the electronic structure of 2,2′-bithiophene.

As compared with absorption spectra of dihexylbithiophenes, spectra of all bithienoquinonoids **2**, **4**, and **5** reflected the highly extended π-electronic conjugation system. HH isomer **2** clearly showed two absorption bands, while both HT and TT isomers **4** and **5** showed one broad band with a shoulder absorption on the point of degenerating. In contrast with an intensive hypsochromic shift of the longest wavelength band for HH dihexylbithiophene **12** from HT isomer **13**, a small bathochromic shift (13 nm) of HH bithienoquinonoid **2** from HT isomer **4** was observed. TT bithienoquinonoid **5** also showed a small bathochromic shift from **4**, affording absorption maxima which are nearly the same as that for HH isomer **2**. Taking the molecular model examinations into consideration, these results indicate that two sets of the steric hindrance between hexyl and dicyanomethylene groups in TT isomer **5**, as well as the aforementioned steric hindrance between hexyl group and sulfur atom in HH isomer **2**, induce deformation of the bithienoquinonoid co-plane to raise their HOMO levels more severely. Although the above phenomena were investigated, those might be caused from relatively small perturbations to the bithienoquinonoid electronic system in a qualitative sense. In other words, it can be concluded that orientation of two 3-hexylthiophene moieties does not affect the electronic transitions for bithienoquinonoid chromophore so much as that for 2,2′-bithiophene chromophore, and that all bithienoquinonoids are substantially planar molecules.

Solvatochromic behavior in the electronic spectra of bithienoquinonoids **2**, **4**, and **5**, which is regarded as an initial indicator of the nonlinear optical activity,[1,2,4] was examined. Due to spontaneous isomerization of TT bithienoquinonoid **5**, all procedures for each spectral measurement were accomplished within a few minutes. Their longest wavelength absorption maxima are given in Table 2.

HH bithienoquinonoid **2** exhibited a bathochromic shift regularly by ca. 10 nm from the corresponding HT isomer **4** in all tested solvents. In both cases of HH and HT isomers, absorption maxima of the main bands varied over 20 nm and shifted to the longer wavelengths with increase of donor number (DN)[9] as a measure of the solvent polarity; hexane < acetonitrile < THF < CH_2Cl_2 < DMF < DMSO, resulting in the greatest electron-acceptable property in DMSO. On the other hand, the main band for TT isomer **5** showed an irregular tendency of bathochromic shift toward DN values differently from that for **2** or **4**, suggesting the most electron-acceptable property in CH_2Cl_2 prior to DMSO. Furthermore, the range of bathochromic shift for **5** in those tested solvents was only 10 nm, which is half as much as that for **2** or **4**, implying that the electron-acceptable property of **5** is smaller than that of **2** and **4**. These results might also be related to a peculiar chemical property of **5** (see below), which was not observed for the other isomers **2** and **4**.

Table 2. Solvatochromic Shift of the Main Bands (λ_{max}/nm) for HH, HT, and TT Bithienoquinonoids

2	**4**	**5**	Solvent
540	530	544	Hexane
543	532	544	Acetonitrile
549	538	549	THF
556	543	545	DMF
559	548	552	DMSO

In consequence, it is indicated that even though the magnitude of steric and electronic effects of hexyl group on the bithienoquinonoid chromophore is not so outstanding nor so different between the respective bithienoquinonoid isomers, the orientation of the 3-hexylthiophene moieties apparently affects the electronic properties of the bithienoquinonoid system.

Studies on Electron-Acceptable Properties of Bithienoquinonoids 2, 4, 5 and the Bromo Derivatives 6 and 7. Cyclic voltammetry of bithienoquinonoids **2**, **4**, and **5** was performed in various solvents. All redox systems were reversible. Their voltammograms in CH_2Cl_2 are shown in Fig. 1 and half-wave reduction potentials are summarized in Table 3, together with those for the corresponding bromo derivatives **6** and **7**.

HH bithienoquinonoid **2** is reduced to dianion $\mathbf{2}^{2-}$, without forming radical anion $\mathbf{2}^{-\bullet}$ even at various scan rates ($\Delta E^1 - \Delta E^2 = \Delta E = 0.00$, also see Fig. 1(a)). This does not indicate the perfect diminution of on-site Coulomb repulsion in $\mathbf{2}^{2-}$, since quaterthienoquinonoid **3** forms the stable radical anion $\mathbf{3}^{-\bullet}$,[1] but rather suggests that radical anion $\mathbf{2}^{-\bullet}$ itself is as unstable as dianion $\mathbf{2}^{2-}$. As can be seen in Figs. 1(b)

Table 3. Half-Wave Reduction Potentials (V) of Bithienoquinonoid Derivatives

	$E^1_{1/2}$	$E^2_{1/2}$	ΔE	(Solvent)
2	−0.15	−0.40	0.25	(THF)
	−0.34	−0.34	0.00	(CH_2Cl_2)
	−0.02	−0.02	0.00	(DMSO)
4	0.01	−0.27	0.28	(THF)
	−0.22	−0.41	0.19	(CH_2Cl_2)
	−0.01	−0.12	0.11	(DMSO)
5	−0.32	−0.71	0.39	(THF)
	−0.24	−0.43	0.19	(CH_2Cl_2)
	−0.07	−0.27	0.20	(DMSO)
6	−0.06	−0.19	0.13	(CH_2Cl_2)
7	−0.08	−0.17	0.09	(CH_2Cl_2)

Measured at the scan rate of 120 mV s^{-1} in the presence of 0.1 M TBA ClO_4 with an Ag/AgCl standard electrode and a platinum working electrode.

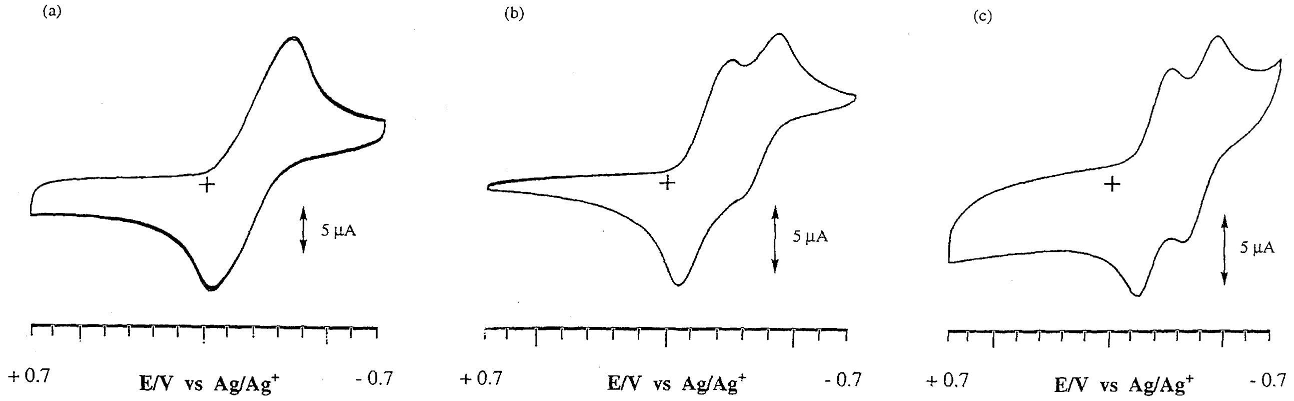


Fig. 1. Cyclic voltammograms of bithienoquinonoids with (a) HH (**2**), (b) HT (**4**), and (c) TT (**5**) orientations in CH_2Cl_2.

and 1(c), HT and TT bithienoquinonoids **4** and **5** proved to be reduced through two one-electron transfer processes to afford the corresponding dianions. The bithienoquinonoid system would recover two 6π-electron thiophene rings, i.e., 2,2′-bithiophene system through re-aromatization in both radical anionic and dianionic structures. The present results apparently indicate that the steric hindrance between hexyl group and sulfur atom of the opposite thiophene ring crucially affects the electrochemical processes and determines the stability of radical anion in the respective bithiophene system with different molecular planarities.

Reduction potentials also varied with both molecular structures and solvents used. In the case of HH bithienoquinonoid **2**, the electron-acceptability outstandingly enhanced in DMSO ($E^1 = -0.02$) than in CH_2Cl_2 ($E^1 = -0.34$). This was the same case for HT isomer **4** ($E^1 = -0.01$ in DMSO, $E^1 = -0.22$ in CH_2Cl_2). It was proved, however, that both HH and HT bithienoquinonoids **2** and **4** exhibited the much greater electron-acceptability in THF (**2**; $E^1 = -0.15$, **4**; $E^1 = -0.01$) than in CH_2Cl_2, contrarily to a previous expectation from a tendency of solvatochromic behaviors in their electronic absorption spectra. Oppositely, TT isomer **5** exhibited the smallest electron-acceptability ($E^1 = -0.32$) in THF and the greatest ($E^1 = -0.07$) in DMSO, in spite of our expectation of the greatest electron-acceptability in CH_2Cl_2 from absorption spectral experiment, resulting in the tendency of electron-acceptable property being the same as the order of DN values; THF < CH_2Cl_2 < DMSO. Moreover, it is worthy of note that THF is effective for stabilizing the radical anion $\mathbf{2}^{-\bullet}$ from HH isomer **2** with sufficient lifetime ($\Delta E = 0.25$), though the property of interaction between $\mathbf{2}^{-\bullet}$ and THF is not clear yet. Although the reduction potentials for these bithienoquinonoids exhibited no common relationship with molecular structures and solvent parameters, the results suggested that the radical anion $\mathbf{5}^{-\bullet}$ and dianion $\mathbf{5}^{2-}$ from TT isomer **5** are less stable than the corresponding reduction products from the other isomers **2** and **4** as a whole.

The bromo derivatives **6** and **7** exhibited very similar tendencies of electrochemical properties, as has been also observed in their absorption spectra (see Experimental), to afford the corresponding dianions $\mathbf{6}^{2-}$ and $\mathbf{7}^{2-}$ via the respective radical anions $\mathbf{6}^{-\bullet}$ and $\mathbf{7}^{-\bullet}$. The stability of $\mathbf{6}^{-\bullet}$ ($\Delta E = 0.13$) and $\mathbf{7}^{-\bullet}$ ($\Delta E = 0.09$) should be ascribed to the other structural factors different from the molecular planarity for π-electronic conjugation of the recovered bithiophene system, since both $\mathbf{6}^{-\bullet}$ and $\mathbf{7}^{-\bullet}$ exist in more twisting conformations than $\mathbf{2}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$, respectively, due to the steric hindrance in the bithiophene system. Taking it into consideration that introduction of bromo substituent to HH isomer **2**, i.e., **6**, formed the stable radical anion $\mathbf{6}^{-\bullet}$, it is likely that the radical electron would be stabilized on the side of the bromothiophene component in the bithiophene system through the mesomeric effect of bromo substituent. Moreover, an inductive effect of bromo substituent would also lower LUMO level of bithienoquinonoid system efficiently, leading to the formation of the stable radical anions from **6** and **7** at the much lower potentials, as compared with **2** and **4**, respectively.

All these results conclude that orientation of 3-hexylthiophene moieties of bithienoquinonoids plays an important role in affecting not only the electronic structure but also the intermolecular interaction between reduction products and solvents. Especially in the case of HH isomer **2**, the redox cycle can be regarded as an electrochemical seesaw which correlates each reduction state with an interconversion between planar and twisting conformations of dinucleic thiophene system. In connection with recent intensive studies on electronic devices by controlling such reversible structure changes, HH bithienoquinonoid **2** with various substituents may provide new candidates as the functional molecular system such as electrochemical switching and as chromic materials like bianthrone derivatives.[10)]

Isomerization of TT Bithienoquinonoid 5 in Solutions. TT bithienoquinonoid **5** proved to exhibit entire stability in solid state but to produce a new species in solution, differently from the other HH and HT isomers **2** and **4** which remain substantially unchanged in solution and in solid state.

The electronic absorption spectra of **5** in various solutions changed via isosbestic points with time, as can be seen from an example of the spectral changes in $CHCl_3$ (Fig. 2). Similarly to the feature of absorption spectral changes, ^{1}H NMR spectra of **5** in $CDCl_3$ also changed with time to give a characteristic peak due to the olefinic protons of a new species **5′**

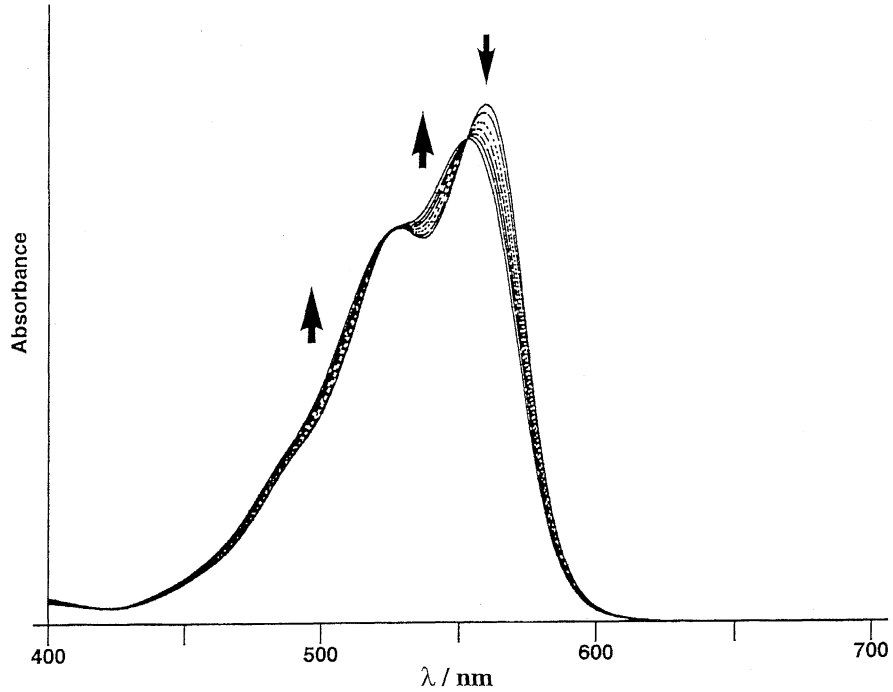


Fig. 2. Electronic absorption spectral changes of TT bithienoquinonoid **5** with 30 min intervals in $CHCl_3$ at 25 °C.

at 7.35 ppm (Fig. 3). The intensity of this newly appearing peak increased regularly with time and reached the maximum within ca. 3 h at room temperature. These phenomena for TT isomer **5** apparently indicate occurrence of an isomerizaton in conformity to a first-order reaction, affording an equilibrium mixture (8—10 : 1) of **5** and **5′** with the very similar electronic structures to each other.

But, it was unsuccessful to isolate the new species **5′** in a pure form for full characterization, because of swift reverse isomerization of **5′** to **5** to give an equilibrium mixture with

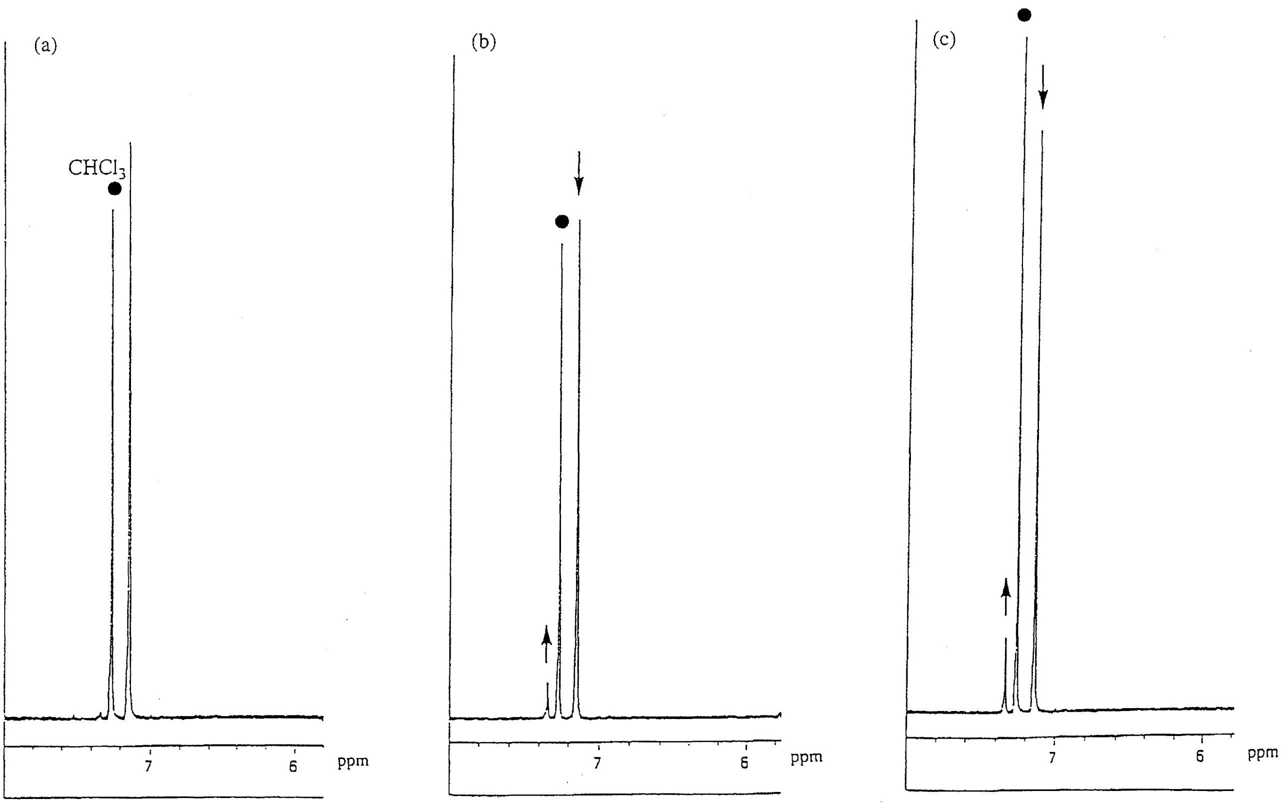
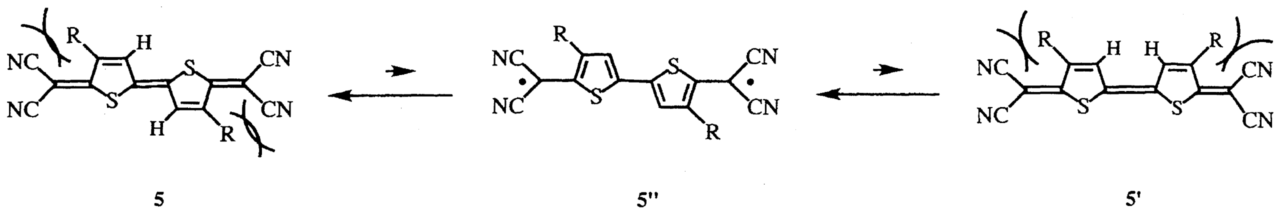


Fig. 3. ^1H NMR spectral changes of TT bithienoquinonoid **5** in $CDCl_3$ at 25 °C; (a) after 1 min, (b) after 30 min, and (c) after 90 min.



Scheme 5.

a greater amount of **5**, even when treated within a minute for spectral measurements. In the ^{1}H NMR spectrum of an equilibrium mixture, all the signals belonging to **5′** were overlapped with those belonging to **5**, except for only one peak due to the olefinic protons which appeared separately from others.

From the facts that (i) the characteristic peak due to olefinic proton (δ = 7.35) of **5′** appears at the lower field than that (δ = 7.15) of **5**, (ii) **5′** possesses the bithienoquinonoid chromophore, and (iii) equilibrium mixture of **5** and **5′** gives the result of the satisfactory mass spectral and elemental analyses comparable to that for the pure substance **5**, the geometrical cisoid isomer for **5′** was deduced to be the most probable product from **5** in a transoid form (Scheme 5 and see Experimental). The lower chemical shift of the olefinic protons of **5′** could be reasonable due to the larger steric compression between these two protons in a cisoid form, as compared with those of **5**.

Isomerization of **5** to **5′** might be driven by two sets of steric hindrance between hexyl and dicyanomethylene groups to proceed via bithiophene system **5″** with a biradical character. It was proved that the spectral changes took place more rapidly in benzene, affording an almost similar result to that in $CHCl_3$. Although it is premature to deduce the isomerization mechanism precisely, it could be concluded that TT isomer **5** passes through the transition state with an extremely small activation energy to another geometrical isomer, as compared with the other HH and HT isomers **2** and **4**.

Conclusion

It was experimentally indicated that orientation of two 3-hexylthiophene moieties in the bithienoquinonoid system does not affect its electronic structure so much as that in the 2,2′-bithiophene system. However, it was proved that such a small perturbation at the ground state due to orientation of two 3-hexylthiophene moieties induces the peculiar features for respective orientational isomers in the bithienoquinonoid system both chemically and electrochemically.

Experimental

The melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were measured on a JASCO FT/IR 7300 spectrophotometer as KBr disks, unless otherwise stated; only significant absorption bands are reported. Electronic spectra were determined in THF solution on a Shimadzu UV-2200A spectrophotometer (sh = shoulder), unless otherwise stated. ^{1}H NMR spectra were taken in $CDCl_3$ solution on JEOL MAC-FX (90 MHz) or JEOL A400 (400 MHz) spectrometers, and were recorded in δ-value with TMS as an internal standard. Mass spectra were recorded with a JEOL JMS-D300 spectrometer operating at 75 eV in a direct inlet system. Cyclic voltammetry was performed on a BAS CV-27. Silica gel (Daiso gel 1001W or Merck 60) and alumina (Merck, Act. II-III) were used for column chromatography. CH_2Cl_2 and $CHCl_3$ were distilled over calcium hydride and THF was distilled from sodium diphenylketyl under argon (Ar) before use. The reactions were followed by TLC aluminum sheets precoated with Merck silica gel F_{254} or with Merck aluminum oxide GF_{254}. Organic extracts were dried over anhydrous sodium sulfate or magnesium sulfate prior to removal of the solvents.

5′-Bromo-3,4′-dihexyl-2,2′-bithiophene (15): To a solution of 2-bromo-3-hexylthiophene (**9**)$^{1)}$ (6.0 g, 24.0 mmol) in THF (100 cm^3) were added drops of butyllithium (1.6 M (1 M = 1 mol dm^{-3}); 16.8 cm^3, 27.0 mmol) in hexane at −80 °C over 15 min under Ar atmosphere. The mixture was stirred for 20 min at −80 °C and then gradually warmed to room temperature. $Fe(acac)_3$ (8.5 g, 24.0 mmol) was added in portions over 10 min at ambient temperature. After being stirred for 2 h, the mixture was diluted with water (300 cm^3), neutralized with 3 M HCl, and extracted with dichloromethane. The extracts were washed with brine and dried. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×50 cm) with hexane to afford a mixture (4.7 g) containing HH bithiophene **12**,$^{1)}$ HT bithiophene **13**,$^{1)}$ and 3-hexylthiophene (**22**). Distillation of the liquid (bp 50 °C/532 Pa, 1 mmHg = 133 Pa) gave **22** (370 mg, 9%), leaving a mixture of HH and HT bithiophenes (3.5 g, 88%) in a flask, its ^{1}H NMR (400 MHz) spectrum showed the ratio of 1 : 1.$^{5)}$

To a solution of 1 : 1 mixture of bithiophenes **12** and **13** (3.5 g, 10.5 mmol) in a mixture of $CHCl_3$ and AcOH (80 cm^3, 1 : 1 v/v), NBS (9.0 g, 5.0 mmol corresponding to the content of HT bithiophene **13**) was added in portions at 0 °C over 15 min. The reaction mixture was stirred for 2 h at 0 °C and then gradually warmed up to ambient temperature. Poured into water, the mixture was extracted with CH_2Cl_2. The extracts were washed successively with brine, dil. aq $NaHCO_3$, and brine. The residue obtained after removal of the solvents was chromatographed on silica gel (4×45 cm) with hexane to afford the HT bromobithiophene **15** (1.9 g, ca. 90% based on **13**) from the first fractions and HH bithiophene **12** (1.78 g, 44.5% based on **9**) from the second fractions. **15**;$^{5)}$ Colorless oil; ^{1}H NMR (90 MHz) δ = 7.13 (1H, d, J = 5 Hz, ThH), 6.88 (1H, d, J = 5 Hz, ThH), 6.78 (1H, s, ThH), 2.72 (2H, t, J = 7 Hz, $\underline{CH_2}$–C_5H_{11}), 2.56 (2H, t, J = 8 Hz, $\underline{CH_2}$–C_5H_{11}), and 1.66—0.89 (22H, m, CH_2–$\underline{C_5H_{11}}$); UV $\lambda_{\max}$ 248 and 303 nm.

5,5′-Dibromo-3,4′-dihexyl-2,2′-bithiophene (16) and 3′,5,5′-tribromo-3,4′-dihexyl-2,2′-bithiophene (23): To a solution of bromide **15** (1.00 g, 2.42 mmol) in a mixture of chloroform and acetic acid (50 : 50 v/v, 100 cm^3), portions of NBS (430 mg, 2.42 mmol) were added at 0 °C over 30 min. After being stirred for 30 min, the mixture was diluted with water and extracted with chloroform. The extracts were washed first with aq 2 M KOH and then with water. The residue obtained after removal of the solvent was chromatographed on silical gel (3.2×5 cm) with hexane to give tribromide **23** (35 mg, 2.5%) as the first fractoin: Pale yellow oil; Mass *m*/*z* 568, 570, 572, and 574 (M^+, M^++2, M^++4, and M^++6 based on ^{79}Br); IR (neat) 2955, 2925, 2855 (CH), 1410, 1465 cm^{-1}; ^{1}H NMR (90 MHz) δ = 6.93 (1H, s, ThH), 2.66 (2H, t, J = 8 Hz, $\underline{CH}_2$–C_5H_{11}), 2.48 (2H, t, J = 8 Hz, $\underline{CH}_2$–C_5H_{11}), and 1.7—0.7 (22H, m, CH_2–$\underline{C_5H_{11}}$). Found: C, 42.35; H, 4.80%. Calcd for $C_{20}H_{27}S_2Br_3$: C, 42.05; H, 4.76%.

The later fractions gave dibromide **16** (1.1 g, 92%): Pale yellow oil; Mass *m*/*z* 490, 492, and 494 (M^+, M^++2, and M^++4 based on ^{79}Br); IR (neat) 2960, 2930, and 2860 cm^{-1} (CH); ^{1}H NMR (400 MHz) δ = 6.85 (1H, s, ThH), 6.72 (1H, s, ThH), 2.62 (2H, t, J = 8 Hz, $\underline{CH}_2$–C_5H_{11}), 2.53 (2H, t, J = 8 Hz, $\underline{CH}_2$–C_5H_{11}), 1.6—1.2 (16H, m, CH_2–$\underline{C}_4\underline{H}_{10}$–$CH_3$), and 0.9—0.6 (6H, m, C_5H_{10}–$C\underline{H}_3$); UV λ_{max} 251 (ε 7400) and 312 nm (sh, ε 10900). Found: C, 49.07; H, 5.59%. Calcd for $C_{20}H_{28}S_2Br_2$: C, 48.79; H, 5.73%.

5,5′-Dibromo-4,4′-dihexyl-2,2′-bithiophene (19): To a solution of 2,5-dibromo-3-hexythiophene (**17**)$^{1)}$ (1.06 g, 3.25 mmol) in THF (30 cm^3) was added a solution of butyllithium (1.6 mol dm^{-3} in hexane, 2.2 cm^3, 3.52 mmol) at −80 °C under Ar atmosphere over 10 min. Fe(acac)$_3$ (1.15 g, 3.25 mmol) was added to the mixture at −80 °C, which was stirred for an additional 20 min and then warmed up to ambient temperature. After being stirred for 2 h, the mixture was diluted with water (300 cm^3), neutralized with 3 M HCl, and extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×60 cm) with hexane to afford the TT bithiophene dibromide **19** (412 mg, 55%) as pale yellow oil: Mass *m*/*z* 490, 492, and 494 (M^+, M^++2, and M^++4 based on ^{79}Br); IR (neat) 3050, 2930, and 2860 cm^{-1} (CH); ^{1}H NMR (400 MHz) δ = 6.78 (2H, s, ThH), 2.53 (4H, t, J = 8.0 Hz, $\underline{CH}_2$–C_5H_{11}), 1.55—1.27 (16H, m, CH_2–$\underline{C}_4\underline{H}_8$–$CH_3$), and 0.96—0.83 (4H, t, J = 8.3 Hz, C_5H_{10}–$C\underline{H}_3$); UV λ_{max} 227 (ε 7800) 251 (ε 8700) 326 (ε 15500), and 354 nm (sh, ε 8100). Found: C, 48.86; H, 5.73%. Calcd for $C_{20}H_{28}S_2Br_2$: C, 48.79; H, 5.73%.

4,4′-Dihexyl-2,2′-bithiophene (14): To a solution of dibromide **19** (600 mg, 1.2 mmol) in THF (30 cm^3) was added $LiAlH_4$ (114 mg, 3.0 mmol) in portions at 0 °C. The mixture was then stirred for 2 h at ambient temperature. After addition of ethyl acetate (10 cm^3), the mixture was poured into iced water, extracted with benzene. The extracts were washed with brine and dried. The residue obtained after removal of the solvents was chromatographed on silica gel (3.2×7 cm) with hexane to give **14** (379 mg, 93%) as pale yellow oil; Mass *m*/*z* 334 (M^+); IR (neat) 2960, 2930, and 2860 cm^{-1} (CH); ^{1}H NMR (400 MHz) δ = 6.97 (2H, s, ThH), 6.76 (2H, s, ThH), 2.57 (4H, t, J = 7.0 Hz, $\underline{CH}_2$–C_5H_{11}), 1.62—1.26 (16H, m, CH_2–$\underline{C}_4\underline{H}_8$–$CH_3$), and 0.95—0.84 (6H, m, CH_3); UV λ_{max} 252 (ε 6400) and 311 (ε 9600). Found: C, 72.08; H, 8.96%. Calcd for $C_{20}H_{30}S_2$: C, 71.80; H, 9.04%.

2,2′-(3,4′-Dihexyl-2,2′5,5′-tetrahydro-2,2′-bithienylidene-5,5′-diylidene)bis(propanedinitrile) (4) and Its 3′-Bromo Derivative 7: To a suspension of sodium hydride (NaH; 98 mg, 60% in oil, 1.94 mmol) in 1,2-dimethoxyethane (8 cm^3) was added malononitrile ($CH_2(CN)_2$, 78 mg, 1.22 mmol) at 0 °C under Ar atmosphere. The mixture was then stirred for 20 min at room temperature. To this solution were added dibromide **16** (252 mg, 0.51 mmol) and $Pd(PPh_3)_4$ (80 mg, 0.51 mmol) successively and the mixture was heated under reflux for 4 h. The mixture was poured into saturated aqueous bromine (40 cm^3) at 0 °C, diluted with cold water (100 cm^3), and then extracted with CH_2Cl_2. The extracts were washed with brine and dried. The residue obtained after removal of the solvent was chromatographed on silica gel (3.2×60 cm) with a mixture of hexane and benzene (1 : 1) to afford the brominated bithienoquinonoid **7**$^{8)}$ (11 mg, 4%) from the initial fractions: Black purple needles (from hexane–benzene); Mp 137—138 °C (decomp); Mass *m*/*z* 539 and 541 (M^+ and M^++2 based on ^{79}Br); IR 2955, 2930, 2855, 2215, and 1500 cm^{-1}; ^{1}H NMR (400 MHz) δ = 7.28 (1H, s, ThH), 3.05 (2H, t, J = 8.5 Hz, $\underline{CH}_2$–C_5H_{11}), 2.94 (2H, t, J = 8.0 Hz, $\underline{CH}_2$–C_5H_{11}), 1.76—0.91 (22H, m, CH_2–$\underline{C}_5\underline{H}_{11}$); UV-visible ($CH_2Cl_2$) λ_{max} 495 (sh, ε 33000), 532 (sh, ε 61500), and 567 nm (ε 78000). Found: C; 58.17; H, 5.29; N, 10.32%. Calcd for $C_{26}H_{27}BrN_4S_2$: C, 57.88; H, 5.04; N, 10.38%.

The later fractions gave HT bithienoquinonoid **4** (49.5 mg, 21%): Black purple needles (from hexane–benzene); Mp 143—145 °C (decomp); Mass *m*/*z* 460 (M^+); IR 2960, 2930, 2855, 2215, and 1500 cm^{-1}; ^{1}H NMR (400 MHz) δ = 7.22 (1H, s, ThH), 7.21 (1H, s, ThH), 2.91 (2H, t, J = 7.5 $\underline{CH}_2$–C_5H_{11}), 2.78 (2H, t, J = 7.1, $\underline{CH}_2$–C_5H_{11}), and 1.78—0.88 (22H, m, CH_2–$\underline{C}_5\underline{H}_{11}$); UV-visible ($CH_2Cl_2$) λ_{max} 500 (sh, ε 38000) and 541 nm (ε 66100). Found: C, 67.93; H, 6.43; N, 12.00%. Calcd for $C_{26}H_{28}N_4S_2$: C, 67.79; H, 6.13; N, 12.16%.

UV-Visible Spectral Data of 4-Bromo Derivative 6$^{1)}$ **in CH_2Cl_2:** λ_{max} 496 (sh, ε 31000), 532 (sh, ε 63000), and 566 nm (ε 71200).

2,2′-(4,4′-Dihexyl-2,2′,5,5′-tetrahydro-2,2′-bithienylidene-5,5′-diylidene)bis(propanedinitrile) (5): By the same way as for **4**, the reaction using NaH (162 mg, 60% in oil, 4.1 mmol), $CH_2(CN)_2$ (112 mg, 1.7 mmol), dibromide **19** (333 mg, 0.68 mmol), 1,2-dimethoxyethane (12 cm^3), and $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) was carried out to give TT bithienoquinonoid **5** (92 mg, 29%): Black purple needles (from hexane–$CHCl_3$); Mp 207—209 °C (decomp); Mass *m*/*z* 460 (M^+); IR 2960, 2930, 2855, 2215, and 1500 cm^{-1}; ^{1}H NMR (400 MHz) δ = 7.15 (2H, s, ThH), 2.91 (4H, t, J = 7.5, $\underline{CH}_2$–C_5H_{11}), and 1.71—0.89 (22H, m, CH_2–$\underline{C}_5\underline{H}_{11}$); UV-visible ($CH_2Cl_2$) λ_{max} 526 (sh, ε 62900) and 554 nm (ε 79200). Found: C, 67.66; H, 6.32; N, 12.01%. Calcd for $C_{26}H_{28}N_4S_2$: C, 67.79; H, 6.13; N, 12.16%.

A sufficient amount of the bromo derivative **8** for full characterization could not be obtained, though MS spectral measurement (*m*/*z* 539 and 541 (M^+ and M^++2)) of the reaction mixture suggested formation of **8**.

Since it was proved that **5** spontaneously isomerizes to give an equilibrium mixture of **5** and **5′** in a ratio of 8—10 : 1 in solutions, flash column chromatography and preparative thin layer chromatography were repeatedly employed for separation to each product. Although the mixture at every stage exhibited the similar MS spectrum (*m*/*z* 460 (M^+) to **5**, the pure material of **5′** for full characterization could not be isolated. Mixtures of **5** and **5′** in ratios of 8 : 1 and 1 : 10 also gave almost the same elemental analyses. Found: C, 67.70; H, 6.36; N, 12.09% for a 1 : 10 mixture. IR spectrum (KBr) of a 1 : 10 mixture of **5** and **5′** was very similar to that of **5**, affording characteristic bands at 2950, 2930, 2855, 2215, and 1450 cm^{-1}.

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