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Solvent Effect on the Bathochromic Shifts of Push-pull Dihexylbithiophenes with Head-to-head and Head-to-tail Orientations

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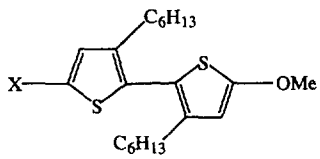
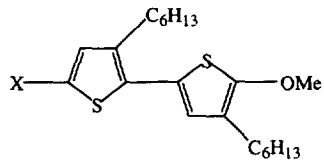
Abstract: The push-pull dihexylbithiophenes with H-H and H-T orientations were synthesized. From the solvent effect of their electronic absorption spectra, it was indicated that the stabilization energies due to solvent polarity were almost the same between these orientational isomers in spite of a large difference of the molecular planarity for conjugation between them.

In recent years, a wide variety of oligomers and polymers composed of 3-alkylthiophene have received much attentions as good candidates for the opto-electronic devices, because of high electron-susceptibility and good processability of the materials.[1] Based on the fact that the hexyl substitutent among long alkyl chains was particularly useful for enhancement of the nonlinear optical (NLO) properties of poly(3-alkylthiophene)s,[2] we previously reported the electronic[3a] and NLO[3b] properties of the symmetrically disubstituted oligo(3-hexylthiophene) derivatives with head-to-head (H-H) orientation. Little attention, however, has been paid for the comparative study on the properties for the smallest unit component of the uni-structured oligo- and poly(3-alkylthiophene)s, i.e., for a pair of orientationally isomeric dialkylbithiophenes, except for dimethylbithiophenes.[4]

In continuation of our investigations on the electronic properties of the well-defined thiophene derivatives, the unsymmetrical H-H (**1**, **2**, **3** and **4**) and head-to-tail (H-T) dihexylbithiophenes (**5**, **6**, **7** and **8**), which bear the methoxy substituent at one end and the more electron-withdrawing ones (X = H, Br, CN, and NO_2) at another end, were synthesized. We describe the electronic absorption spectral behaviors of these orientationally isomeric dihexylbithiophenes with the push-pull character as well as the solvent effect on their wavelength shifts.



1: X = H
2: = Br
3: = CN
4: = NO_2

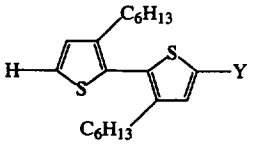


5: X = H
6 = Br
7: = CN
8: = NO_2

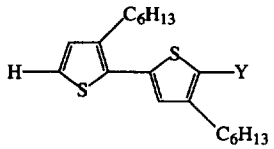
Synthetic method by the cross-coupling reaction of each component convenient for the unsymmetrical bithiophenes[5] resulted in poor reproducibility and yet in low yields especially for the H-H dihexylbithiophenes. Therefore, the title H-H (**1** - **4**) and H-T (**5** - **8**) methoxybithiophenes were synthesized from the starting materials of H-H (**9**) and H-T (**10**) dihexylbithiophenes which can be easily prepared in large quantities from the same material, 3-hexylthiophene, according to our recently developed procedure.[6]

The bithiophenes **9** and **10** were brominated with N-bromosuccinimide (NBS) in a mixture of acetic acid and chloroform (1:1)[3a] to afford the corresponding H-H (**11**; 60%) and H-T (**12**; quant) bromobithiophenes which were transformed by a copper-catalyzed Williamson synthesis[7] to the methoxybithiophenes **1**[8] (62%) and **5**[8] (39%).

The methoxybithiophenes **1** and **5** were again brominated with NBS to give the bromomethoxybithiophenes **2**[8] (49%) and **6**[8] (quant). The cyanomethoxybithiophenes **3**[8] (45%) and **7**[8] (79%) were obtained from the reaction[3a] of the corresponding bromides **2** and **6** with copper(I) cyanide (CuCN). Nitration of the methoxybithiophenes **1** and **5** with nitric acid (HNO_3) in a mixture of acetic anhydride and THF (2:1)[9] gave the methoxynitrobithiophenes **4**[8] (66%) and **8**[8] (63%).



9: Y = H
11: = Br



10: Y = H
12: = Br

The electronic spectra of the methoxybithiophenes **1** - **8** were observed in various solvents and their longest wavelength absorption maxima in THF were plotted to give Fig. 1.

Introduction of alkyl substituents into 2,2'-bithiophene would reduce the molecular planarity for conjugation between thiophene rings due to the steric repulsion between alkyl chains and sulfur atom in the opposite thiophene ring, generally resulting in the hypsochromic shift for the dialkylbithiophenes from 2,2'-bithiophene.[4] In contrast with a large difference in hypsochromic shift between methyl (270 nm)[4] and hexyl (**9**: 244 nm in $CHCl_3$) substituents for the H-H bithiophenes, the H-T bithiophenes exhibited the very similar absorption maxima between methyl (302 nm same as that for 2,2'-bithiophene)[4] and hexyl (**10**: 297 nm in $CHCl_3$) substituents, suggesting that the H-T dihexylbithiophene **10** exists in an almost planar conformation similarly to 2,2'-bithiophene. In the case of the push-pull bithiophenes, the H-H derivatives (**4**; 378 nm in hexane) also exhibited the large hypsochromic shift from the non-alkylated methoxynitrobithiophene (408 nm)[5]. The H-T isomers (**8**; 414 nm in hexane), however, showed a small bathochromic shift, probably because of an elevation of HOMO in consequence of distortion of the molecular planarity due to an additional steric strain between methoxy and hexyl substituents.

As is seen in Fig. 1, both of the orientationally isomeric bithiophenes showed the maxima in the much longer wavelength regions depending on the substituent X by 20 nm up to 150 nm compared with the corresponding H-H (**9**) and H-T (**10**) bithiophenes. Their maxima shifted to the longer wavelengths exponentially with an increase of

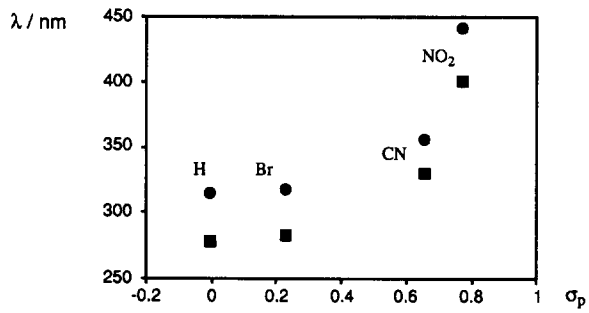


Fig. 1. Correlation of electronic absorption maxima (λ/nm) with substituent constants (σ_p) of the H-H (■) and H-T (●) methoxybithiophenes.

the electron-withdrawing abilities of the substituents; X = H < Br < CN << NO_2, clearly indicating that the methoxybithiophenes **1** - **8** possess the polarized structure properties which stabilize the excited state of the bithiophene chromophore efficiently arising from the electronic interaction between the substituents, OMe and X, at the ends.[5] It is interesting to note that the H-H bithiophenes always showed their maxima at the shorter wavelengths by ca. 40 nm from the corresponding H-T isomers, seemingly independent of the substituent X.

In order to ascertain the push-pull character which is believed to be a measure of NLO effect,[1-3] the solvatochromic properties of the methoxybithiophenes were examined. The transition energies corresponding to the longest wavelength absorption bands were plotted against the solvent parameter, π^* scale,[10] which is employed as the scale of polarity and polarizability of the solvent, to give Fig. 2.

As is evident from Fig. 2, both of the H-H and H-T methoxybithiophenes exhibited the negative slopes with good linear correlations between the transition energies and the π^*-values, clearly indicating that the absorption maxima shift to the longer wavelengths with increasing the π^*-values, i. e., positive solvatochromism. With increasing the electron-withdrawing abilities of the substituents the corresponding slopes become larger, reflecting the greater contribution of the polarized structure property at the excited states in these push-pull bithiophenes.

It is worthy of note that in spite of the large difference of the molecular planarity between H-H and H-T bithiophenes, the outstandingly high similarity of the solvatochromic behavior between them was observed. Especially in the cases of the cyano- (H-H **3** and H-T **7**) and the nitro- (H-H **4** and H-T **8**) methoxybithiophenes, the almost same negative slopes for the solvatochromic correlations[5] (r = -0.956 / -0.961 and -0.996 / -0.995) were

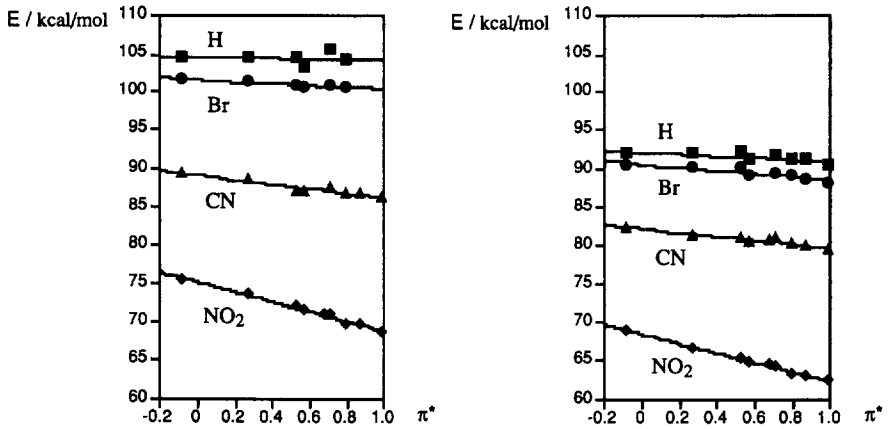


Fig. 2. Correlation of the transition energies with the π^* scale for the substituted H-H (left) and H-T (right) methoxybithiophenes.

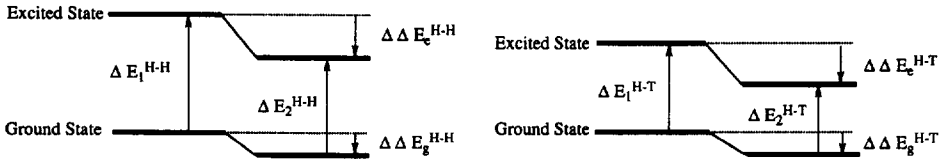


Fig. 3. Stabilization energies of the push-pull H-H (left) and H-T (right) bithiophenes due to solvent effects.

obtained, respectively. In other words, the stabilization at the excited state ($\Delta\Delta E_e$) due to the solvent effect is larger than that at the ground state ($\Delta\Delta E_g$) and yet the net stabilization energies, $\Delta\Delta E_e - \Delta\Delta E_g$, are almost the same between these pairs of H-H and H-T methoxybithiophenes, respectively, as illustrated in Fig. 3. This result indicates that the molecular planarity for conjugation at the ground state does not affect the solvent effect on the stabilization of the push-pull type of bithiophenes, though it is premature to deduce the reason for the present phenomenon.

Further comparative study on the redox and NLO properties of these orientationally isomeric methoxybithiophenes are now in progress.

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8. All new compounds gave satisfactory analytical and spectral data.
   Selected ^{1}H NMR (90 MHz, $CDCl_3$, δ) data are as follows: **1** (Pale yellow oil) 7.23 (d, J=5Hz, 1H, ThH), 6.92 (d, J=5Hz, 1H, ThH), 6.07 (s, 1H, ThH), 3.88 (s, 3H, OCH_3), 2.59-2.30 (m, 4H, $C\underline{H}_2C_5H_{11}$), 1.25-1.06 (m, 16H, $CH_2(C\underline{H}_2)_4CH_3$), 0.88 (m, 6H, $(CH_2)_5C\underline{H}_3$). **2** (Pale yellow oil) 6.88 (s, 1H, ThH), 6.06 (s, 1H, ThH), 3.87 (s, 3H, OCH_3), 2.53-2.30 (m, 4H, $C\underline{H}_2C_5H_{11}$), 1.54-0.79 (m, 22H, $CH_2C_5\underline{H}_{11}$). **3** (Pale yellow oil) 7.44 (s, 1H, ThH), 6.10 (s, 1H, ThH), 3.90 (s, 3H, OCH_3), 2.52 (t, J=7.4Hz, 2H, $C\underline{H}_2C_5H_{11}$), 2.39 (t, J=7.7Hz, 2H, $C\underline{H}_2C_5H_{11}$), 1.55-1.06 (m, 16H, $CH_2(C\underline{H}_2)_4CH_3$), 0.86 (br t, J=6Hz, 6H, $(CH_2)_5C\underline{H}_3$). **4** (Yellow oil) 7.77 (s, 1H, ThH), 6.32 (s, 1H, ThH), 3.94 (s, 3H, OCH_3), 2.56 (br t, J=8Hz, 4H, $C\underline{H}_2C_5H_{11}$), 1.79-0.79 (m, 22H, $CH_2C_5\underline{H}_{11}$). **5** (Pale yellow oil) 7.09 (d, J=5.3Hz, 1H, ThH), 6.88 (d, J=5.3Hz, 1H, ThH), 6.65 (s, 1H, ThH), 3.90 (s, 3H, OCH_3), 2.71 (t, J=6.7Hz, 2H, $C\underline{H}_2C_5H_{11}$), 2.47 (t, J=7.6Hz, 2H, $C\underline{H}_2C_5H_{11}$), 1.6-0.8 (m, 22H, $CH_2C_5\underline{H}_{11}$). **6** (Pale yellow oil) 6.83 (s, 1H, ThH), 6.60 (s, 1H, ThH), 3.90 (s, 3H, OCH_3), 2.64 (t, J=6.4Hz, 2H, $C\underline{H}_2C_5H_{11}$), 2.45 (t, J=7.3Hz, 2H, $C\underline{H}_2C_5H_{11}$), 1.6-0.8 (m, 22H, $CH_2C_5\underline{H}_{11}$). **7** (Pale yellow oil) 7.38 (s, 1H, ThH), 6.79 (s, 1H, ThH), 3.93 (s, 3H, OCH_3), 2.78 (t, J=6.8Hz, 2H, $C\underline{H}_2C_5H_{11}$), 2.48 (t, J=6.6Hz, 2H, $C\underline{H}_2C_5H_{11}$), 1.6-0.8 (m, 22H, $CH_2C_5\underline{H}_{11}$). **8** (Yellow oil) 7.72 (s, 1H, ThH), 6.91 (s, 1H, ThH), 3.95 (s, 3H, OCH_3), 2.72 (t, J=6.7Hz,2H, $C\underline{H}_2C_5H_{11}$), 2.48 (t, J=7.3Hz, 2H, $C\underline{H}_2C_5H_{11}$), 1.7-0.8 (m, 22H, $CH_2C_5\underline{H}_{11}$).
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