Photophysical properties of bis(2,2'-bithiophene-5-yl)benzenes

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The synthesis of three kinds of bis(2,2'-bithiophene-5-yl)benzenes (1,2-, 1,3- and 1,4-bis(2,2'-bithiophene-5-yl)benzene; o-PhBT₂, m-PhBT₂ and p-PhBT₂) and analyses of their photophysical properties are reported. The electronic structures were also studied by the molecular orbital (MO) method. It was found that the extension of π -conjugation varies with the substitution mode (o-, m-, or p-), which in turn influences the absorption, fluorescence and transient absorption spectra. The unique behaviour of o-PhBT₂ was interpreted in terms of its lowest unoccupied MO (LUMO) pattern, in which π -orbitals on the adjacent sulfur atoms in each bithienyl moiety can have considerable overlap.

In recent years, oligomers possessing π -conjugation, especially oligothiophene, have received much attention as model compounds for related conjugated polymers. Since these oligomers are well defined chemical systems, investigations of their sizedependent properties aids understanding of the properties of conjugated polymers and these have been extensively studied, both theoretically and experimentally.¹ In particular, studies on their radical cations and dications have produced a better understanding of the nature of the polarons and bipolarons in polythiophenes, that are responsible for their electrical and optical properties.^{1a,b} Moreover, the photophysical properties of their neutral state have been comprehensively studied by several groups.² These photophysical properties have a close relationship to their electronic structures. In these studies, state order is an important subject.

Most studies on oligothiophene were carried out in highly dilute solution in order to suppress any intermolecular interactions. However, in conjugated polymers, intermolecular processes are important, in phenomena such as charge transport and relaxation of the photo-excited state is much affected by higher-order structure. By linking two oligothiophenes it will become possible to observe clearly the intermolecular processes between them. Moreover, Aviram has proposed the idea of a molecular electronic device using the oligothiophene dimer.³ The dimer system composed of oligothiophenes has also been studied. We have already succeeded in the synthesis of homogeneous and inhomogeneous oligothiophene dimers, linked by trimethylene, in order to understand the intermolecular processes in polythiophene.⁴ Kanemitsu et al. have studied several kinds of oligothiophene dimers as a quasi-onedimensional system, separated by a potential-energy barrier.⁵ Orthogonally fused oligothiophenes have been synthesized by Diaz et al.⁶ based on Aviram's hypothetical structure. Kuroda et al. have synthesized oligothiophene dimers bridged by anthracene.7

In the present study, three kinds of phenylene-bridged oligothiophene dimers (PhBT₂s) were synthesized in which two 2,2'-bithiophene-5-yl (bithienyl) groups are bridged by *o*-, *m*and *p*-phenylene groups, respectively. Their molecular structures are depicted in Fig. 1. The dimer system bridged by phenylene groups has been studied with respect to the interaction between chromophores such as porphyrin.⁸ However, the π -conjugation of the bithienyl group in the present compounds should be somewhat extended owing to the connection with the phenylene group. In this sense, these compounds can be model oligomers for a copolymer composed of thienylene and phenylene.⁹ The degree of extension of the π conjugation was tuned by the substitution in the phenylene moieties. This idea originated from the fact that the phenylene moieties are expected to induce a remarkable difference in the electronic structures of these compounds. Their photophysical properties were investigated in detail and compared with those of the reference compounds and oligothiophenes. Their electronic structures were also analysed theoretically.

Experimental

Materials

1,2-, 1,3- and 1,4-bis(2,2'-bithiophene-5-yl)benzene (o-PhBT₂, m-PhBT₂ and p-PhBT₂) were synthesized following the procedure described below. 2,2'-Bithiophene (BT), 2,2':5'2"-terthiophene (TT) and 2,2'-bithiophene-5-ylbenzene (PhBT) were used as the reference compounds in the present study. BT was purchased from Aldrich and recrystallized from methanol. TT and PhBT were synthesized by the Ni-catalysed Grignard coupling reaction¹⁰ and purified by column chromatography on SiO₂, followed by recrystallization. The other chemicals





*m***-PhBT₂**. Under a N₂ atmosphere, an anhydrous ether solution (15 ml) of thienyl magnesium bromide prepared from 9.8 g of 2-bromothiophene and 1.5 g of magnesium was added to a mixture of 1,3-dibromobenzene (5.7 g) and NiCl₂[dppp] (0.32 g) suspended in anhydrous ether. After stirring for 24 h under reflux, water was added to the reaction mixture and the crude product was extracted. The crude product was purified by SiO₂ column chromatography followed by recrystallization from methanol, giving 5.7 g of 1,3-dithienylbenzene (yield 81%).

6.0 g of 1,3-dithienylbenzene was dissolved in 148 ml of a 1:1 mixture of chloroform and acetic acid. 10 g of *N*-bromosuccinimide was added and then stirred for 4 h at room temperature.¹¹ After removal of solvent, the crude product was recrystallized from *n*-hexane to give 8.5 g of α -brominated compound (yield 86%). This compound was applied to the Grignard cross-coupling reaction with thienyl magnesium bromide, following the same procedure as that for the synthesis of 1,3-dithienylbenzene. *m*-PhBT₂ was obtained after purification by SiO₂ column chromatography followed by recrystallization from *n*-hexane–benzene (yield: 9%); ¹H-NMR (400 MHz, CDCl₃) δ 7.04 (2H, dd, J = 5, 4 Hz), 7.17 (2H, d, J = 4 Hz), 7.22 (2H, dd, J = 4, 1 Hz), 7.24 (2H, dd, J = 5, 1 Hz), 7.28 (2H, d, J = 4 Hz), 7.37–7.41 (1H, m), 7.50–7.52 (2H, m), 7.80–7.81 (1H, m), EIMS *m/z*; 406 (M⁺).

o-PhBT₂. o-PhBT₂ was synthesized from 1,2-dibromobenzene and 2-bromothiophene following the same procedure as for the synthesis of m-PhBT₂. ¹H-NMR (400 MHz, CDCl₃) δ 6.82 (2H, d, J = 4 Hz), 6.99 (2H, dd, J = 4, 5 Hz), 7.04 (2H, d, J = 4 Hz), 7.13 (2H, dd, J = 4, 1 Hz), 7.19 (2H, dd, J = 1, 5 Hz), 7.37 (2H, m), 7.52 (2H, m). EIMS m/z; 406 (M⁺).

p-PhBT₂. *p*-PhBT₂ was synthesized by the Suzuki reaction.¹² Under an N₂ atmosphere, 0.492 g of *p*-phenylene bis(2,2'-dimethytrimelthylene)boronate was synthesized following the literature,¹³ 0.980 g of 5-bromo-2,2'-bithiophene and 0.228 g of tetrakis(triphenylphosphine)-palladium were added to the 40 ml of an equivolume mixture of 1,2-dimethoxyethane and 2 mol 1⁻¹ Na₂CO₃ aqueous solution. After stirring for 87 h under reflux, the crude product was extracted with benzene. The crude product was purified by SiO₂ column chromatography followed by recrystallization from chloroform and *n*-hexane-benzene, giving 0.047 g of *p*-PhBT₂ (yield: 6%). ¹H-NMR (400 MHz, CDCl₃) δ 7.04 (2H, dd, J = 5, 4 Hz), 7.16 (2H, d, J = 4 Hz), 7.22 (2H, dd, J = 4, 1 Hz), 7.23 (2H, dd, J = 5, 1 Hz), 7.26 (2H, d, J = 4 Hz), 7.61 (4H, s), EIMS *m*/*z*; 406 (M⁺).

Optical measurements

The absorption spectra were measured with a Shimadzu UV-2200 spectrophotometer. The fluorescence and fluorescence excitation spectra were measured with a Shimadzu RF-503A spectrofluorometer. These spectra were obtained at 20 °C for CH₂Cl₂ solution $(10^{-5}-10^{-4} \text{ mol } 1^{-1})$. The fluorescence quantum yields were estimated using quinine sulfate dissolved in 0.5 mol 1^{-1} sulfuric acid aqueous solution as standard. For fluorescence measurements at 77 K, a solution in methanol–ethanol = 1/1(v/v) was used (*ca.* $10^{-5} \text{ mol } 1^{-1}$). Before the solutions were cooled to 77 K, fluorescence measurements were carried out under identical conditions at room temperature.

Fluorescence lifetimes were measured by the single-photon counting method using an argon ion laser (Spectra-Physics, BeamLok 2060-10-SA), a pumped Ti:sapphire laser (Spectra Physics, Tsunami 3950-L2S, 1.5 ps fwhm) with a pulse selector (Spectra Physics, Model 3980), a third harmonic generator (GWU-23PS) and a streakscope (Hamamatsu Photonics, C4334-01). In the present study, all the samples were excited at 368 nm.

The transient-absorption spectra in the visible and near-IR region (350–1000 nm) were measured using FHG (266 nm) of an Nd:YAG laser (Quanta-Ray, GCR-130, fwhm 6 ns) as an excitation source. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60) was used as a monitor light. An Si-PIN photodiode (Hamamatsu Photonics, S1722-02) detector attached to a monochromator (Ritsu MC-10N) was employed. The output signal from the detector was recorded with a digitizing oscilloscope (Hewlett-Packard 55410B) and analysed by a personal computer. All the measurements were carried out in a 1 cm quartz cell after 15 min of argon bubbling.

Results

Absorption and emission

The absorption spectra of the three types of PhBT₂s are shown in Fig. 2, together with those of the reference compounds. Structureless absorption bands assigned to the π - π * transition were observed in *m*- and *p*-PhBT₂. In the spectrum of *o*-PhBT₂, the observed absorption band was accompanied by a shoulder on the lower energy side. Absorption maxima and molar absorption coefficients for the PhBT₂s are listed in Table 1.

The absorption maxima of the PhBT₂s were observed at lower energy than for BT; the energy of absorption maximum is a measure of the spatial extent of π -conjugation. The degree of the redshift from BT was in the order *p*-PhBT₂ > *m*-PhBT₂ > *o*-PhBT₂. It has been reported, for oligothiophenes, that the energies of the absorption maxima change inversely proportional to the conjugation length.² These results have been interpreted by the spatial extension of the singlet excited state over the molecule.^{1e} Supposing that the conjugation length can be represented by the number of double bonds (*n*), the peak energy (*E*) of the unsubstituted oligothiophenes in the literature^{1a,2} can be described by

$$E = \frac{7.32}{n} + 2.26\tag{1}$$

which gives *n* values of 4.7, 5.8 and 8.0 for *o*-PhBT₂, *m*-PhBT₂ extent of π -conjugation in those molecules. Incidentally, n = 5.3 was estimated for PhBT.



Fig. 2 Top: absorption spectra of (a) o-PhBT₂, (b) m-PhBT₂ and (c) p-PhBT₂. Bottom; those of (a) BT, (b) TT and (c) PhBT. All spectra were recorded in CH₂Cl₂ at room temperature.

Table 1 Photophysical data for $PhBT_{2}s$ in $CH_{2}Cl_{2}$ at room temperature

	absorbance		fluorescence	
compound	$\lambda_{\rm max}/{\rm nm}$	$\epsilon_{\rm max}/l \ {\rm mol}^{-1} \ {\rm cm}^{-1}$	$\lambda_{ m max}/ m nm^a$	$\Phi_{ m F}$
o-PhBT ₂ m-PhBT ₂ p-PhBT ₂	324.6 350.8 390.8	3.27×10^4 5.02×10^4 5.06×10^4	482 402, 422 448, 474	0.14 0.13 0.69

^{*a*} The italicized wavelength correspond to the band maximum, the other designates another distinct band (see Fig. 2).

The fluorescence spectra of the PhBT₂s are shown in Fig. 3, together with those of their reference compounds. In contrast to the absorption spectra, structured fluorescence bands were observed in the spectra of m- and p-PhBT₂s, although that of o-PhBT₂ was structureless and observed at the lowest energy region in contrast with the highest energy absorption band. The shape of the fluorescence band, particularly its vibronic structure, changes in oligothiophenes with the number of thiophene rings. The fluorescence bands observed for o-, mand p-PhBT₂ bore resemblance to those of BT, TT and pentathiophene, respectively.^{2b} The fluorescence quantum yields $(\Phi_{\rm F})$ estimated for the PhBT₂s are listed in Table 1. These values are higher than those of BT (0.013-0.026) and TT (0.054-0.07);^{2b} the quantum yield increases with the number of thiophene rings in oligothiophenes. Note that a remarkable increase in the yield was observed in p-PhBT₂. This yield is rather higher than those of pentathiophene and hexathiophene (0.28-0.44).²



Fig. 3 Top: fluorescence spectra of (a) o-PhBT₂, (b) m-PhBT₂ and (c) p-PhBT₂. Bottom: those of (a) BT, (b) TT and (c) PhBT. All spectra were recorded in CH₂Cl₂ at room temperature.

The fluorescence and fluorescence excitation spectra in an ethanol-methanol glass matrix were observed in PhBT2s and PhBT at 77 K and room temperature, and are shown in Fig. 4. A considerable increase in the fluorescence intensity at 77 K was observed in m-PhBT₂, as well as in PhBT. Since the vibrational resolution in both the fluorescence and excitation spectra generally increases in comparison with that at room temperature, these results indicate that suppression of the inter-ring rotation affected the quantum efficiencies in m-PhBT₂ and PhBT. On the other hand, the fluorescence intensity of p-PhBT₂ did not much increase, although considerable increase in vibrational resolution was seen. The fluorescence excitation bands of p-PhBT₂ shifted to lower energy. In contrast, no remarkable difference was observed between the fluorescence spectra of o-PhBT₂ at 77 K and room temperature, apart from an increase in the fluorescence intensity. The fluorescence excitation spectrum at room temperature showed a shoulder peak, being more clearly resolved at 77 K.

The fluorescence decay curves of the PhBT₂s in CH_2Cl_2 are given in Fig. 5. The decay curves of m- and p-PhBT₂s could be fit by a single exponential, implying a typical monomolecular decay. In contrast, that of o-PhBT₂ was fit by a double exponential. The transient fluorescence was also measured for the methanol-ethanol solutions of PhBT2s at both room temperature and 77 K. The lifetimes obtained are listed in Table 2, where similar behaviour is seen. The fluorescence decay kinetics of o-PhBT₂ did not depend on the concentration $(10^{-4}-10^{-5} \text{ mol } 1^{-1})$. Moreover, similar kinetics was also observed in the glass matrix at 77 K, thus ruling out a bimolecular process. In general, the double-exponential model has been used to describe the existence of two emissive species.¹⁴ Hence, in o-PhBT₂, two emissive species should exist, although the detail of these is currently not known. Rotational conformers around the inter-ring bond, for instance, can be considered to rationalize the kinetics, because large steric hindrance is expected in o-PhBT₂, as discussed later. The lifetimes obtained for o- and p-PhBT₂s did not depend on temperature but that for m-PhBT₂ increased on lowering the temperature. This corresponds to an increase in quantum yield. The lifetimes of the m- and p-PhBT₂s did not change much with the solvent, whereas that of o-PhBT₂ in methanol-ethanol solutions decreased.

The experimental values of the radiative rate constants $(k_{\rm R, exp})$ in Table 2 were estimated from fluorescence lifetime (τ) and quantum yield ($\Phi_{\rm F}$):

$$k_{\rm R, \, exp} = \frac{\Phi_{\rm F}}{\tau} \tag{2}$$

On the other hand, $k_{\rm R, calc}$ can be estimated from the Stickler-Berg equation $(3a)^{15}$ from the absorption and fluorescence spectra

$$k_{\rm R, \ calc} = \frac{8 \times 2303\pi cn^2}{N} \langle \tilde{\nu}^{-3} \rangle_{\rm AV}^{-1} \int \frac{\epsilon(\tilde{\nu})}{\tilde{\nu}} \, \mathrm{d}\tilde{\nu} \tag{3a}$$

$$\langle \tilde{v}^{-3} \rangle_{\rm AV}^{-1} = \frac{\int I(\tilde{v}) \, \mathrm{d}\tilde{v}}{\int \tilde{v}^{-3} I(\tilde{v}) \, \mathrm{d}\tilde{v}}$$
(3b)



Fig. 4 Fluorescence and fluorescence excitation spectra of (a) o-PhBT₂, (b) m-PhBT₂, (c) p-PhBT₂ and (d) PhBT at room temperature (······) and 77 K (-----) in methanol-ethanol



Fig. 5 Fluorescence decay curves of (a) o-PhBT₂, (b) m-PhBT₂ and (c) p-PhBT₂ recorded in CH₂Cl₂ at room temperature

where $\langle \tilde{v}^{-3} \rangle_{AV}^{-1}$ was estimated from the fluorescence spectra shown in Fig. 3 and $\int [\epsilon(\tilde{v})/\tilde{v}] d\tilde{v}$ from the lowest $\pi - \pi^*$ absorption bands shown in Fig. 2, the bands being extracted by means of curve fitting with Gaussian functions. This equation can be applied when the absorption is sufficiently intense and the absorption and fluorescence spectra are the mirror image of each other. Since the latter condition is not completely met for PhBT₂s, some deviation should be contained in the calculated values. However, rather good agreement between the experimental and calculated values have been reported for oligothiophenes, in spite of similar absorption and fluorescence spectra.^{2b,16}

For o-PhBT₂, two emissive species could exist, as discussed earlier. In such case, the estimation of $k_{\rm R, cale}$ based on the Strickler-Berg equation was not acceptable in the strict sense. However, the observed absorption and fluorescence bands of o-PhBT₂ that should be the superimposed spectra of two species were not so broad in comparison with those of the *m*and *p*-PhBT₂s. The spectra of two emissive species should thus bear close resemblance to each other. Therefore, the $k_{\rm R}$ values estimated from the observed spectra should be close to those of two species. The calculated rate constant values are also listed in Table 2. The calculated values for PhBT₂s are in reasonable agreement with the experimental results, in which the smaller rate constant of o-PhBT₂ corresponds to the calculated value. These results indicate the one-to-one correspondence of the ground state to the lowest singlet excited state.

Triplet excited state

The transient absorption spectra of the $PhBT_2s$ and PhBT are shown in Fig. 6. These transient absorption bands were

assigned to the triplet-triplet $(T_n \leftarrow T_1)$ absorption. It has been reported for oligothiophenes that the triplet-triplet absorption maxima shifted to lower energy, inversely proportional to n, the number of double bonds.^{2b} Beljonne et al. have reported that the lowest triplet excited state (T_1) of oligothiophenes is strongly confined and the higher triplet state is delocalized (T_n) , then the shift in triplet-triplet absorption is attributed to the delocalization of the T_n state.^{1e} The transient absorption band of p-PhBT₂ was composed of a single absorption band around 620 nm, closely resembling that of pentathiophene.^{2b} The m-PhBT₂ transient absorption band was observed around 450 nm and was accompanied by a shoulder peak around 570 nm. The spectra were quite similar to those of TT^{2b} and PhBT, indicating a similar spatial extent of the triplet excited states $(T_1 \text{ and } T_n)$ of *m*-PhBT₂, TT and PhBT. On the other hand, different behaviour was observed for o-PhBT₂: the absorption maximum was observed around 460 nm, as in m-PhBT₂, but an additional peak was observed at longer wavelength. Incidentally, in the PhBT₂s, phosphorescence could not be observed, similarly to the oligothiophenes.

Theoretical analysis

As described earlier, there should be various rotational conformers in PhBT₂s. In order to examine the geometries of PhBT₂s, molecular orbital (MO) calculations were carried out in the semi-empirical level (AM1 approximation¹⁷) using the MOPAC program.¹⁸ The potential barrier for rotation around the inter-ring bond has been studied extensively for BT and its derivatives.¹⁹

The potential-energy curves plotted for the rotation around thiophene-thiophene (Th-Th) and thiophene-phenylene

 Table 2
 Fluorescence lifetimes of the PhBT₂s

	CH ₂ Cl ₂ solution at room temperature			methanol-ethanol solution				
compound	τ/ns	$k_{\rm R, exp}/10^9 {\rm s}^{-1}$	$k_{\rm R, \ calc}/10^9 \ {\rm s}^{-1}$	τ/ns (rt)	τ/ns (77 K)			
o-PhBT ₂ m-PhBT ₂ p-PhBT ₂	0.71, 1.49 0.23 0.97	0.19, 0.94 0.57 0.71	0.22 0.46 0.35	0.46, 1.22 0.24 0.93	0.50, 1.22 0.41 0.93			
	(a)	0.6	(b) 0.15	(c) 0.4	(d)			



Fig. 6 Transient absorption spectra of (a) o-PhBT₂, (b) m-PhBT₂, (c) p-PhBT₂ and (d) PhBT observed at 250 ns (\bullet) and 2.5 μ s (\bigcirc) after excitation



Fig. 7 Potential-energy curves for the rotation around Ph–Th (\bullet) and Th–Th (\blacksquare) rings

(Th–Ph) rings obtained in the present calculation are shown in Fig. 7. Other structural parameters than θ were all energetically optimized. It is seen that the twisted *anti*-conformer was most stable for Th–Th rotation and that the barrier for Th–Ph rotation is larger than that for Th–Th. It has been reported that the *anti*-conformer is the more stable, based on the NMR spectroscopy²⁰ and gas-phase electron diffraction.^{19d} The potential barrier for the rotation around Th–Th rings was calculated to be *ca.* 0.5 kcal mol⁻¹. This value is similar to the reported value,^{19b} but rather smaller than those determined by NMR²⁰ and by *ab initio* calculation.^{19c}

A large potential barrier for the rotation around Ph–Th rings should be expected for o-PhBT₂ because of steric hindrance. In order to examine that potential barrier, MO calculations for o-dithienylbenzene were also carried out. After total energetical optimization, two kinds of dihedral angle (θ_L and θ_R) were made to change. Other structural parameters than θ were all energetically optimized. In Fig. 8, the potential profiles vs. θ_R (dihedral angle between the right-hand Th and the Ph rings) for a couple of fixed values of θ_L (that between the left-hand Th and the Ph rings) are given. It is seen that the configuration in which the sulfur atoms on the two thiophene rings become in close proximity is the most stable and that the potential barrier to any other conformation is rather large (ca. 5 kcal mol⁻¹) compared with that of the Th–Ph rotation in Fig. 7 (ca. 0.9 kcal mol⁻¹).

With respect to the PhBT₂s, all the structural parameters were energetically optimized except for the assumption of C_s symmetry in *o*-PhBT₂. The dihedral angles between the thiophene rings obtained by this optimization were 152°, 156° and 153° for *o*-, *m*- and *p*-PhBT₂, respectively. The dihedral angles between Th–Ph rings were 44°, 28° and 20° for *o*-, *m*- and *p*-PhBT₂, respectively.

Although the present MO calculations are only qualitative, correlation between the photophysical properties of the PhBT₂s and their electronic structures can be found by an



Fig. 8 Potential-energy curves for rotation around Ph–Th rings of *o*-dithienylbenzene. The dihedral angle $\theta_{\rm L}$ (see text) is fixed at -45° (\blacktriangle), -90° (\bigcirc) and -135° (\bigcirc).

approximation-invariant manner, as described in what follows: The highest occupied (HO) and lowest unoccupied (LU) MO patterns of PhBT₂s were all of pseudo π -type for each ring, as illustrated in Fig. 9. These patterns of *p*-PhBT₂ are of a π -type, delocalized over the whole molecule. Moreover, the aromatic and quinoid characters are induced by inphase overlapping at the HOMO and the LUMO, respectively.²¹ On the other hand, for *m*-PhBT₂, the nodal plane cuts the π -conjugation in the centre of the phenylene rings in both the HOMO and the LUMO. Hence π electrons of *m*-PhBT₂ are delocalized within the bithienyl unit and a vinyl part in the *m*-phenylene moiety, and aromatic and quinoid characters exist within this spatial extent.

In the HOMO of o-PhBT₂, π -lobes exist on the bithienyl and the carbon atoms bonded to bithienyl groups. Therefore, the relationship between the electronic properties of o-PhBT₂ and a bithiophene dimer bridged by a vinylene group would be of interest. However, the absorption and the fluorescence spectra of the latter are notably different from those of the former⁵ and such difference could be attributed to the fixation of the two bithienyl groups in the neighbourhood of o-PhBT₂. In fact, in o-PhBT₂, since the distance between adjacent sulfur atoms is rather small (2.444 Å), the LUMO on the two sulfur atoms can be overlapped, as depicted in Fig. 10. This result indicates that the interaction between two bithienyl groups cannot be neglected in its excited state. This interaction of two bithienyl groups can be considered as one of the reasons for the structureless absorption and emission.

Discussion

Structureless absorption and structured fluorescence spectra were observed for *m*- and *p*-PhBT₂. In a class of non-rigid aromatic molecules, the diffuse absorption band and the structured emission band are observed and interpreted as showing that the structure in the ground state is non-planar and nonrigid and that in the excited state is more planar and rigid.²² Such absorption and fluorescence spectra have also been observed for various oligothiophenes.² These spectra have been interpreted as follows: The HOMO and the LUMO of oligothiophenes have aromatic and quinoid character, respectively¹⁶ and, hence, the inter-ring bonds gain double bond character by HOMO–LUMO electronic transition resulting in a more planar and rigid molecular structure. Similarly, the redshift and increase in the vibrational resolution of



Fig. 9 Frontier MO patterns of (a) $\mathit{o}\text{-PhBT}_2$, (b) $\mathit{m}\text{-PhBT}_2$ and (c) $\mathit{p}\text{-PhBT}_2$

Fig. 10 The S-S overlapping (pointed by an arrow) in the LUMO of o-PhBT₂: (a) Pattern seen from the same direction as Fig. 9 and (b) from the right-hand side

m- and *p*-PhBT₂s in a glass matrix at 77 K can be explained by the molecular structure becoming more planar in the ground state. The change in the fluorescence spectra of m- and p-PhBT₂s is similar to those of TT and pentathiophene.^{2b} In *m*- and *p*-PhBT₂s, the fluorescence excitation spectra at 77 K and fluorescence spectra at room temperature form a good mirror image, as seen in Fig. 4. These results indicate that these molecules in the lowest singlet excited state at room temperature and the ground state at 77 K have similar planarity. However, the observed behaviour of o-PhBT₂ was quite different. The shape of the fluorescence band resembles that of BT at room temperature, as seen in Fig. 3. However, it has been reported that BT showed a well resolved spectrum at 77 K.^{2b} This indicates that the diffused absorption and emission bands observed for o-PhBT₂ do not come from the inter-ring rotation of bithienyl moieties.

The absorption, fluorescence and transient absorption of mand p-PhBT₂s can be interpreted in terms of the extent of π -conjugation, as discussed in the theoretical analysis. Incidentally, 'cutting' of the π -conjugation observed in *m*-PhBT₂ has also been seen in the polymer prepared by its electrochemical polymerization.9c For o-PhBT2, unusual behaviour was observed in the absorption, fluorescence and transient absorption. It can be considered that the structureless band is not only due to rotations around the inter-ring bond but also to quite different characteristics of the excited state of o- $PhBT_2$ from those of *m*- and *p*-PhBT₂. The result of the Strickler-Berg equation suggested one-to-one correspondence of the ground state with the lowest singlet excited state. The energy gap estimated from the crossing points of the absorption and fluorescence were 3.04, 3.22 and 2.93 eV at room temperature and 3.04, 3.18 and 2.84 eV at 77 K for o-, m- and p-PhBT₂, respectively. A decrease in energy gap with decrease in temperature was observed for m- and p-PhBT₂. These results indicate that the π -conjugation is more extended at low temperature because of the planarity of the structures. On the other hand, the energy gap of o-PhBT₂ did not change. The energy gap of o-PhBT₂ is intermediate between those of mand p-PhBT₂ at both room temperature and 77 K. Hence, the π -conjugation in o-PhBT₂ is more extended than that of m-PhBT₂. However, this extension is not due to an increase in the planarity in the excited state, as shown by the structureless fluorescence spectra. The overlap of π orbitals on the adjacent sulfur atoms indicated that the excited state of o-PhBT₂ could be extended somewhat by interaction between the excited and the unexcited bithienyl moieties. The structureless fluorescence and decrease in lifetime with the solvent polarity suggested a contribution from the charge-transfer state to the singlet excited state.

Conclusion

Three types of PhBT₂s were successfully synthesized and their photophysical properties were investigated. Their photo-**2360** J. Chem. Soc., Faraday Trans., 1998, Vol. 94 physical properties differed considerably depending on the substitution mode in the phenylene moieties. It is shown from the MO patterns of these compounds that such a change is due to a remarkable difference in the extent of the π -conjugation. In particular, the result for *o*-PhBT₂ was quite different from those of *m*- and *p*-PhBT₂. The electronic structure of *o*-PhBT₂ is rather unique and requires more attention. The LUMO pattern of *o*-PhBT₂ indicated that its excited state can be delocalized by interaction between the excited and the unexcited bithienyl moieties. The structureless fluorescence and decrease in lifetime with solvent polarity suggested a contribution from the charge-transfer state to the singlet excited state.

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