Intermolecular Interactions in Conjugated Oligothiophenes. 2. Quantum Chemical Calculations Performed on Crystalline Structures of Terthiophene and Substituted Terthiophenes

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Quantum-chemical calculations are used to investigate the influence of intermolecular interactions on the absorption spectra of unsubstituted terthiophene (TT) as well as 3,3′′-dimethyl-2,2′:5′,2′′-terthiophene (DMTT) and 3′,4′-dibutyl-2,2′:5′,2′′-terthiophene (DBTT). The semiempirical ZINDO/S method is employed to calculate the energy of the electronic transitions of a single molecule in this crystalline structure and of interacting molecules in subcrystalline forms of various sizes (2 and 4 molecules). For all molecules investigated, intermolecular interactions lead to a splitting (Davydov's splitting) of the lowest optical singlet transition compared to that calculated for an isolated molecule. These results are interpreted through the use of the excitonic model. The splitting of the first electronic transition is very sensitive to the different intermolecular distances and orientations found in the crystalline structures of each molecule. TT shows an important excitonic effect on the first allowed transition whereas the splitting is less important for substituted terthiophenes. The spectral shifts caused by intermolecular interactions are compared with those induced by conformational changes toward planarity for the isolated molecules in the crystals (packing effects). The results clearly show that the excitonic effect is mainly responsible for the optical properties of TT in its aggregated form whereas, for substituted terthiophenes, the conformational change suggested in part 1 of this series of papers is the major cause of the red shifts observed in their absorption bands following aggregation.

1. Introduction

In the last 20 years, new organic conjugated polymers have been developed as electrical conductors and active materials in various electronic and optoelectronic devices.[1] For instance, poly(paraphenylenevinylene) (PPV)[2−4] and polythiophenes[5−9] have shown good electrooptical properties. For this reason, a wide variety of experimental investigations have been performed on these systems. The electronic properties of oligothiophenes in the solid state[10−20] have particularly retained the attention since the intermolecular interactions induce an important excitonic effect (Frenkel exciton) combined with possible charge transfers and polaron pairs.

Since it is rather difficult to ascribe with certainty the various peaks found in the optical spectra recorded in condensed phases, theoretical methods could be useful to determine the effect of intermolecular interactions on the absorption bands observed experimentally. In the literature, one can find several theoretical analyses dealing with the effect of the chromophore length[21] as well as the presence of lateral substituents[22−27] on the electronic properties and conformations of oligothiophene derivatives. These calculations have provided valuable information about the structure−property relationships of these compounds. For instance, an interesting relationship between the rotational energy barriers of model bithiophene derivatives and the occurrence (or not) of thermochromism in the parent polymers has been established.[28] However, these calculations have been performed on isolated molecules (representing dilute solutions or the incorporation of the oligomers in inert matrixes).

The intermolecular interactions occurring for oligothiophenes in condensed media have not been studied much by theoretical methods,[29] but a few calculations involving PPV-oligomer models have been reported in the literature.[30−32] It is shown that, in high-symmetry cofacial configuration, intermolecular interactions induce a splitting (Davydov splitting) of the first excited singlet state (S_1) in two states (S_1 and S_2, called Frenkel exciton states). According to these calculations, the first singlet−singlet electronic transition ($S_1 \leftarrow S_0$) is lower in energy and forbidden by symmetry compared to that of the isolated molecules. On the other hand, the second singlet−singlet electronic transition ($S_2 \leftarrow S_0$) is blue-shifted and allowed. The consequence of this behavior for a highly symmetric sandwich-type dimer is a blue shift of its simulated absorption spectrum. The largest difference in energy between S_1 and S_2 excited states occurs for an intermolecular distance of 3.5 Å and where the molecules are perfectly parallel. This energy gap rapidly becomes narrower if the intermolecular distance increases or if the symmetry of the system is reduced by an increase of the molecular disorder. The exciton model has been well described by Kasha et al.[33−35]

To gain a better understanding of the structure−property relationships of polythiophenes, molecular mechanics coupled to Monte Carlo calculations have been performed on these macromolecules[36,37] and on the crystalline structure of a polythiophene model.[38] These studies have provided valuable information about the structure of a free polymer chain and about the influence of the motion of the lateral chains on the stacking effect of substituted polythiophenes in their crystalline forms.

Up to now, the electronic interactions occurring for oligothiophene derivatives in condensed media have been investigated

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by modeling the aggregated forms of unsubtituted systems. As discussed in part 1 of this series of papers,[39] the presence of lateral groups induces important changes in the optical properties of substituted oligothiophenes following aggregation. We report in this second part a theoretical analysis of the electronic properties of terthiophene (TT) as well as two alkyl-substituted terthiophenes, namely, 3,3′′-dimethyl-2,2′:5′,2′′-terthiophene (DMTT) and 3′,4′-dibutyl-2,2′:5′,2′′-terthiophene (DBTT), in their respective aggregated forms. Because intermolecular interactions involve a very large array of associated molecules and because each derivative in its aggregated form has its own molecular conformation, the X-ray data for these compounds have been used. Since the formation of aggregates is obtained in a way similar to that for the preparation of single crystals used for the crystallographic analysis and since the optical properties involving the oligothiophenes in their aggregated forms are very similar to those in the solid state,[39] the molecular structure of the aggregates is expected to be rather similar to the crystalline structures. The electronic excited-state energy of different clusters (1−4 molecules) based on the crystalline structures has been calculated using the ZINDO/S (Zerner intermediate neglect of differential overlap for spectroscopy) semiempirical method.

These results show that, for all the terthiophene derivatives studied, intermolecular interactions induce an excitonic splitting of the first excited singlet state. The energy differences between these new states are very sensitive to the relative position of the interacting molecules in the crystal and to the size of the aggregate (number of interacting molecules). For TT, the sandwich type aggregate exhibits an important Davydov splitting, which becomes larger as the number of molecules in the configuration is increased, causing a blue shift of the first allowed singlet−singlet transition ($S_2 \leftarrow S_0$). On the other hand, a head-to-tail arrangement of the molecules does not significantly change the energy of the $S_1 \leftarrow S_0$ electronic transition of the isolated molecules. Since the conformational change caused by the packing effect is relatively small for TT,[40] the red-shift of the $S_1 \leftarrow S_0$ electronic transition of the isolated molecules caused by the increase of planarity is small compared to the large blue shift of the $S_2 \leftarrow S_0$ transition of the aggregated form. This behavior results in an overall blue shift of the absorption spectrum of TT in its aggregated form. For the substituted derivatives, the excitonic splitting becomes much less important due to a larger disorder in the crystal structures induced by the presence of the lateral chains and by the twisted conformation of each molecular unit. On the other hand, conformational changes caused by the packing effect in the solid state are much more important for these molecules compared to that of TT.[40] This leads us to conclude that the red shift observed in the absorption spectra of these molecules, following aggregation, is mainly due to conformational changes toward planarity. The structures of the molecules investigated are displayed in Figure 1.

2. Methodology

The crystalline structures of terthiophene (TT),[41] 3,3′′-dimethyl-2,2′:5′,2′′-terthiophene (DMTT),[42] and 3′,4′-dibutyl-2,2′:5′,2′′-terthiophene (DBTT)[43] have been reproduced according to these X-ray data. Few neighbored cells have been built to ensure that all intermolecular interactions are considered. A homemade program has been used to convert the Cartesian coordinates to hyperchem input files.

Theoretical calculations were performed, on the basis of crystalline data, using the Hyperchem package, release 5.0, for Windows 95 from Hypercube, Inc. The electronic transition energies and their related intensities have been calculated within the framework of the ZINDO/S (Zerner intermediate neglect of differential overlap for spectroscopy) Hartree−Fock semiempirical method including configuration interactions (CI). ZINDO/S is a modified INDO method parametrized to reproduce UV/visible spectroscopic transitions.[44,45] The electron-repulsion integrals were evaluated using the Mataga−Nishimoto formula. CI is chosen in a way to ensure the absence of changes in the spectroscopic parameters when increasing the size of the CI for the size of clusters studied in this paper (1−4 molecules).

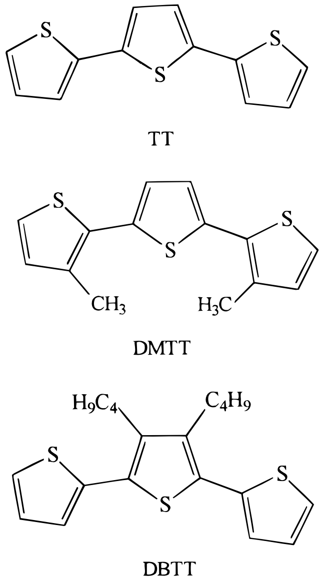

Figure 1. Molecular structure and nomenclature used of the molecules investigated.

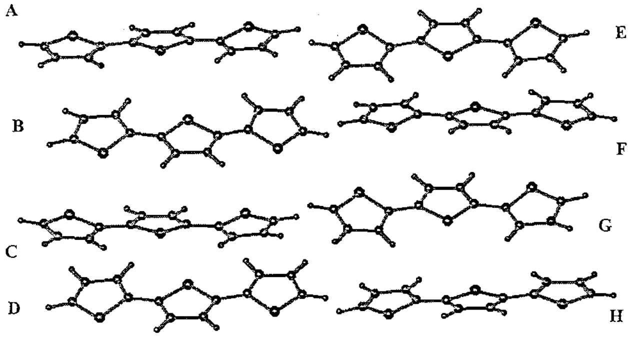

Figure 2. Crystalline structure of TT. Labels (A−H) are used to identify each molecule in subcrystalline structures used for the ZINDO/S calculations.

Simulations of the absorption spectra were done using a Gaussian band centered at the transiton energy with a bandwidth of 1000 cm^{-1}. For the aggregated forms, the sum of each Gaussian normalized with the oscillator strength calculated for each transition has been done.

3. Results and Discussion

3.1. Terthiophene (TT). The unit cell of the crystalline structure of TT is reproduced in Figure 2.[41] In this arrangement, the molecules form two distinct parallel orientations, one formed by molecules A, C, F, and H and a second orientation involving molecules B, D, E, and G. These two orientations are not perpendicular to each other but form an angle of ∼45°. Each terthiophene unit in the crystal is nearly planar in an anti conformation with a dihedral angle between thiophene rings (θ)

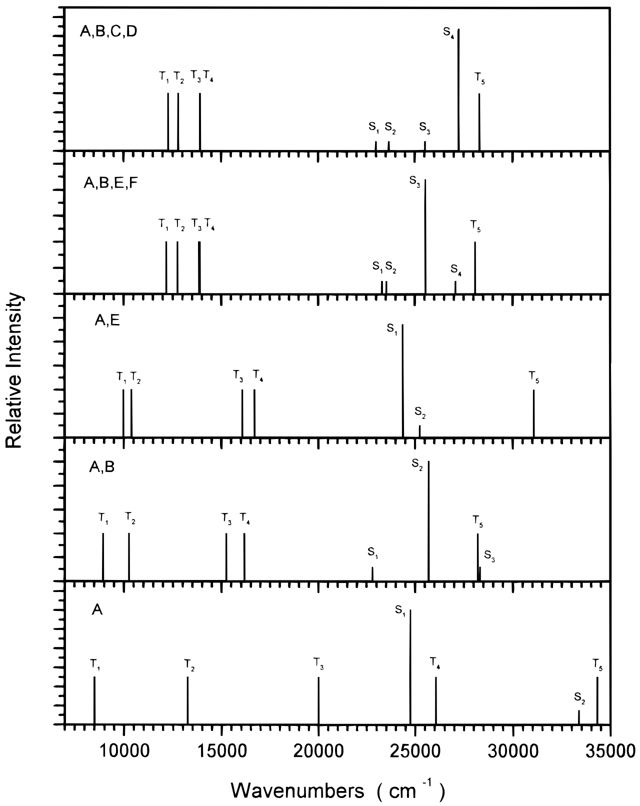

Figure 3. Calculated energies of the singlet−singlet and singlet−triplet electronic transitions of TT. The intensities of the forbidden (or weakly allowed) transitions are increased arbitrarily to be visible. Letters on each window represent the TT molecules (see Figure 2) involved in the crystalline forms investigated in the ZINDO/S calculations (from 1 to 4 molecules).

TABLE 1: Energy (Relative to the S_0 State), Oscillator Strength, and Molecular Orbitals (MO) Involved in the First Excited Singlet States of Subcrystalline Forms of TT

subcrystalline forms[a]	excited singlet states	energy [cm^{-1} (eV)]	f[b]	MO[c]
A	S_1	24 728 (3.07)	1.2024	H → L
A,B	S_1	22 784 (2.83)	0.0814	H → L H → L + 1
	S_2	25 681 (3.18)	2.5107	H − 1 → L H − 1 → L + 1
A,E	S_1	24 355 (3.02)	2.3701	H → L H − 1 → L + 1
	S_2	25 227 (3.13)	0.0090	H → L + 1 H − 1 → L
A,B,E,F	S_1	23 288 (2.89)	0.3627	H → L
	S_2	23 518 (2.92)	0.0017	H → L + 1
	S_3	25 530 (3.17)	4.3984	
	S_4	27 071 (3.36)	0.0260	H − 2 → L + 1
A,B,C,D	S_1	22 983 (2.85)	0.0086	H → L
	S_2	23 646 (2.93)	0.0187	H − 1 → L
	S_3	25 517 (3.16)	0.0200	H − 2 → L + 1
	S_4	27 241 (3.38)	6.3736	

[a] See Figure 2 for the nomenclature. [b] Oscillator strength. [c] H for HOMO (highest occupied molecular orbital) and L for LUMO (lowest unoccupied molecular orbital).

TABLE 2: Comparison between Observed and Calculated Absorption Spectra for Various Oligothiophene Species

molecule		expt[a] (cm^{-1})	calcd[b] (cm^{-1})	Δ[c] (cm^{-1})
TT	free (147°)	28 350	26 291	2059
	A	26 800	24 728	2072
	A,B,C,D	24 500	22 983	1517
		32 000	27 241	4759
DMTT	free (118°)	29 300	31 786	2486
	A	27 050	27 490	440
	A,B,C,D	28 200	27 451	749
			28 780	580
DBTT	free (105°)	29 940	32 010	2070
	A	27 250	25 265	1985
	A,B,C,D	27 250	25 250	2000
			26 001	1249

[a] Wavenumber of the absorption maximum in fluid *n*-decane solution at 298 K (free), isolated in *n*-decane matrix at 77 K (A) and in the aggregate forms at 77 K (A,B,C,D). [b] Wavenumber of the absorption spectrum as calculated from ZINDO/S. [c] Difference between experimental and calculated results.

of ∼172−174°. The increase in planarity, compared to the conformation calculated for the isolated molecules in the gas phase or in dilute solution ($\theta \sim 147°$[40]), is due to the packing effect occurring in the solid phase. The energies of some excited singlet and triplet states for a single molecule and for several molecular aggregates as calculated from ZINDO/S are displayed in Figure 3. The energy values of the first singlet excited states and the oscillator strength (f) of the corresponding singlet−singlet electronic transitions as well as the molecular orbitals (MO) involved in these transitions are reported in Table 1. It is worth mentioning that the absolute values of the transition energies as calculated by ZINDO/S for the "free" or isolated (A) molecules are generally within a 2000 cm^{-1} bracket when compared with the experimental results; see Table 2. Indeed, the ZINDO/S energy values correspond only approximately to the 0,0 electronic transitions of the molecules in the gas phase (more acurately it is the vertical transition between the two states) whereas the optical spectra are recorded in solution (where the 0,0 vibronic peak is not well resolved) and rigid media. However, since the goal of this work is to investigate the effect of the intermolecular interactions on the molecular electronic properties, we will focus our discussion on the spectral shifts resulting from the aggregation process rather than on the exact energy values of the electronic transitions.

The calculated electronic spectrum of a single molecule of TT in this crystalline structure (A from Figure 3) exhibits a first allowed singlet−singlet transition ($S_1 \leftarrow S_0$) located at 24 728 cm^{-1} ($f = 1.2024$) and a second weakly allowed transition ($S_2 \leftarrow S_0$) appearing at 33 358 cm^{-1}. The $S_1 \leftarrow S_0$ electronic transition calculated for the same molecular structure but with a dihedral angle of 147° (simulating the expected conformation of free TT in solution[40]) gives an energy value of 26 291 cm^{-1} with a slightly smaller oscillator strength ($f = 1.113$). The increase in the transition energy (1563 cm^{-1}) and the small decrease of f are caused by the partial break of resonance between π orbitals along the oligomer long axis due to the decrease in the dihedral angle. This shift is very close in energy to that observed experimentally between the excitation spectrum of the molecules isolated in a *n*-decane matrix at 77 K (nearly planar conformation) and the absorption spectrum recorded at room temperature in the same solvent (1550 cm^{-1}; see Table 1 and Figure 4 in part 1 of this series of paper[39] and Table 2 of this paper). The $S_2 \leftarrow S_0$ electronic transition is less affected (blue shift of 709 cm^{-1} for the twisted conformer), showing the smaller dependence of this singlet−singlet transition on conformational changes. A similar behavior has been observed experimentally as shown in Figure 4 of part 1.[39] One could also perform a ZINDO/S calculation on the basis of an HF/3-21G* molecular optimization[40] for obtaining the transition energy of the "free" molecule, but we have shown that the results obtained are within the 2000 cm^{-1} bracket discussed above for all molecules investigated in this paper. We then decided to

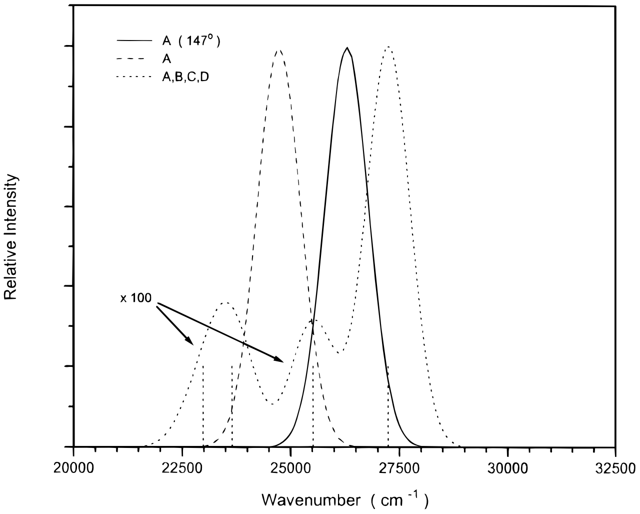

Figure 4. Simulated absorption spectra of TT. Letters in the legend represent the TT molecules (see Figure 2) involved in the crystalline form calculated. The spectrum of the free molecule (147°) is obtained as discussed in the text. The normalized transition energies of the tetramer are also indicated.

compare in Table 2 experimental transition energies with calculated ones all based on the crystalline structures with the dihedral angle as the only varying parameter for the "free" molecule.

The first triplet state (T_1) appears at a very low energy (A in Figure 3), which is consistent, according to the energy gap law, with the absence of phosphorescence found for TT and other oligothiophene derivatives. Indeed, the high values of the triplet quantum yield of these molecules would favor the occurrence of phosphorescence.[46,47] One can also see that the T_4 excited state is lying just above the S_1 state in agreement with theoretical results reported elsewhere[21] and with the experimental observation of an activated energy for the deactivation pathway of the S_1 state through the triplet state T_4.[47] One can note that triplet states discussed throughout this paper are for the planar conformation (A) and that the energy level of the T_1 state is lower than that calculated[47,48] for the more twisted conformations expected in solution.

To investigate the effect of the intermolecular interactions on the different excited states of the isolated molecules, first we have considered the interactions between two adjacent molecules (dimer). As illustrated in Figure 2, two types of association should exist in the TT crystal: a sandwich-type and a head-to-tail interactions. The electronic properties of the A,B dimer (sandwich-type configuration) and the A,E dimer (head-to-tail configuration) have been calculated (see Figure 3 and Table 1). Results show that the interaction between molecules A and B induces a splitting of the S_1 excited state of the isolated molecule (A) in two states. The $S_1 \leftarrow S_0$ electronic transition of the sandwich-type dimer is weak and lower in energy whereas the $S_2 \leftarrow S_0$ electronic transition is much intense and is blue shifted compared to the allowed electronic transition found in the isolated molecule. This excitonic splitting (Davydov splitting) is similar to those observed for oligomer models of PPV[30,32] and is consistent with theoretical models developed by Kasha et al.[33-35] For a perfect parallel and symmetric TT sandwich-type dimer, a C_{2h} symmetry is observed. For this symmetry group, the $S_1 \leftarrow S_0$ electronic transition between totally symmetric S_0 and S_1 singlet states (A_g) is forbidden by symmetry while the $S_2 \leftarrow S_0$ electronic transition between S_0 (A_g) and S_2 (B_u) singlet states is allowed. One can see that, even if the TT sandwich-type dimer is not perfectly symmetric, the selection rules discussed above are not much relaxed. Figure 3 shows that, after aggregation, the red shift of the S_1 excited state (1944 cm^{-1}) is larger than the blue shift of its S_2 excited state (953 cm^{-1}). Moreover, Table 1 shows that the $S_1 \leftarrow S_0$ electronic transition involves a mixing of the HOMO (H) $\rightarrow$ LUMO (L) and $H \rightarrow L + 1$ molecular orbitals while the $S_2 \leftarrow S_0$ electronic transition involves a mixing of the $H - 1 \rightarrow L$ and $H - 1 \rightarrow L + 1$ molecular orbitals. It is worth mentioning that ZINDO/S calculations have shown that the energy difference between H and $H - 1$ molecular orbitals (0.17 eV) is larger than that calculated between L and $L + 1$ molecular orbitals (0.09 eV). The same behavior has been reported for oligomer models of PPV.[32]

Figure 3 shows that the head-to-tail interactions (dimer A,E) barely affect the electronic properties of the isolated molecule. Indeed, the $S_1 \leftarrow S_0$ electronic transition is allowed and is slightly red-shifted compared to that of the isolated molecule. On the other hand, the S_2 excited singlet state is slightly higher in energy compared to the S_1 excited state of the isolated molecule whereas the $S_2 \leftarrow S_0$ electronic transition of the dimer A,E is forbidden.

Two distinct tetramers have also been considered in these calculations, molecules A, B, E, and F which form a type of tetramer involving sandwich and head-to-tail types of interaction and molecules A, B, C, and D which present only a sandwich type of interaction. As illustrated in Figure 3, the tetramer A,B,E,F exhibits a excitonic splitting similar to that of the dimer A,B confirming the above statement that head-to-tail interactions do not induce an important Davydov splitting. However, one can see that the excitonic splitting induces by the tetramer A,B,E,F is slightly smaller than that observed for the dimer A,B. This behavior might imply that head-to-tail interactions partly annihilate the cofacial interactions. In contrast, the tetramer A,B,C,D shows a more important excitonic splitting than that calculated for the dimer A,B. Indeed one can see that the more intense singlet–singlet electronic transition ($S_4 \leftarrow S_0$) of this tetramer is blue shifted by 2513 cm^{-1} compared to the $S_1 \leftarrow S_0$ electronic transition of molecule A (see Figure 3 and Table 1). This shift is much larger than that calculated for the dimer A,B (953 cm^{-1}). On the other hand, the ($S_1 \leftarrow S_0$) singlet–singlet transition of the A,B,C,D aggregate which is also forbidden appears at about the same energy as that of the sandwich-type dimer. Thus the excitonic splitting ($S_4 - S_1$) of the tetramer (4258 cm^{-1}) is much higher than that of the dimer (2897 cm^{-1}). This is a well-known result that the excitonic splitting is more important for larger sandwich-type aggregates.[32-35]

To compare the theoretical results with the optical properties of TT, Figure 4 displays the absorption spectrum of single molecules isolated (having the crystalline conformation) (A) and free A (147°) and that of the A,B,C,D aggregate. Table 2 compares those calculated data with experiments. One can see that the absorption band of an isolated molecule in the crystal is red-shifted compared to that of the "free" molecule. This is caused by the increase in planarity found in the solid state due to the packing effect. But the intermolecular interactions present for TT in its aggregated form (as exemplified by the tetramer A,B,C,D) induce an overall blue shift of its absorption band compared to that recorded in solution (A with $\theta = 147°$). One can also observe in Figure 4 the red-shifted bands caused by intermolecular interactions, which have very low intensities. These theoretical results show a good correlation with the optical spectra of TT reported in part 1 of this series of paper.[39] However the blue shift of the $S_4 \leftarrow S_0$ transition following aggregation (A,B,C,D), as calculated by the ZINDO/S method,

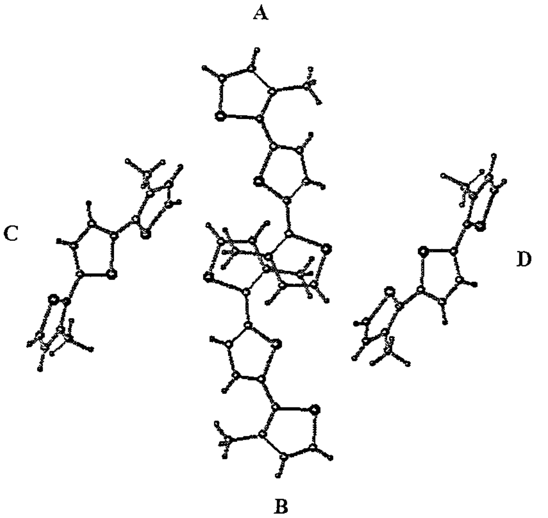

Figure 5. Crystalline structure of DMTT. Labels (A−D) are used to identify each molecule in the subcrystalline structures used for the ZINDO/S calculations.

is smaller than that measured from the absorption spectra. Indeed, a maximum wavenumber of 27 241 cm^{-1} is predicted theoretically compared to 32 000 cm^{-1} observed experimentally (see Table 2). This might imply that the actual aggregate of TT involves more than four molecules.

3.2. 3,3″-Dimethyl-2,2′:5′,2″-terthiophene (DMTT). The crystalline structure of DMTT,[42] as shown in Figure 5, is much different than that found for TT (see Figure 2). Indeed molecules A and B are parallel but cofacial interactions are limited to one thiophene ring whereas molecules C and D are also parallel. The structure of the single molecule in the solid state is also different than that of TT. Indeed each molecule of DMTT adopts a twisted conformation of about 30° from planarity whereas a mixture of *syn-gauche* and *anti-gauche* conformers is observed in the crystal. However, the conformation found for DMTT in the solid state is more planar than that predicted from HF/3-21G* ab initio calculations for a "free" molecule ($\theta = 118°$).[40]

The excited singlet and triplet states of the single molecules and of various aggregates are displayed in Figure 6, and the properties of their first singlet−singlet transitions are reported in Table 3 and compared with experimental one in Table 2. For the isolated molecule, the $S_1 \leftarrow S_0$ electronic transition is intense ($f = 1.113$) and is located at 27 490 cm^{-1}. This transition energy is higher than that reported above for TT whereas its oscillator strength is smaller. This is a consequence of the twisted conformation found for DMTT in the solid state compared to the nearly planar one for TT. The $S_1 \leftarrow S_0$ electronic transition of DMTT having the same structural parameters but with $\theta = 118°$ (free) appears at a much higher energy (31 786 cm^{-1}) giving rise to a blue shift of 4296 cm^{-1} compared to the A form. This shift is much higher than that measured between the absorption and excitation spectra of DMTT in solution and in the *n*-decane matrix at 77K (2250 cm^{-1}). We believe that this behavior arises from an overestimation of the $S_1 \leftarrow S_0$ transition energy for the very twisted conformers as calculated by the ZINDO/S method. This was observed before for heavily twisted conformers.[49] One can see in Table 2 that the calculated first singlet transition energy for the free molecule is again in the ~2000 cm^{-1} bracket compared to the experiment as observed for TT. For the isolated molecule and the aggregated form (A,B,C,D), the difference between the observed and calculated transition energies is smaller (~500 cm^{-1}).

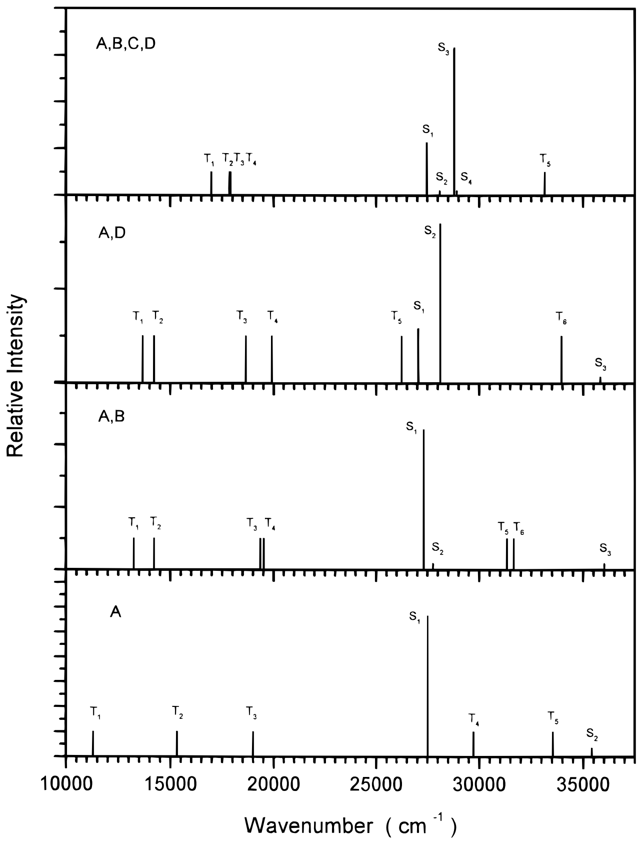

Figure 6. Calculated energies of the singlet−singlet and singlet−triplet electronic transitions of DMTT. The intensities of the forbidden (or weakly allowed) transitions are increased arbitrarily to be visible. Letters on each window represent the DMTT molecules (see Figure 5) involved in the crystalline forms investigated (from 1 to 4 molecules).

TABLE 3: Energy (Relative to the S_0 State), Oscillator Strength, and Molecular Orbitals (MO) Involved for First Excited Singlet States of Subcrystalline Forms of DMTT

subcrystalline forms[a]	excited singlet states	energy [cm^{-1} (eV)]	f[b]	MO[c]
A	S_1	27 490 (3.41)	1.1330	$H \rightarrow L$
A,B	S_1	27 291 (3.38)	2.2449	$H \rightarrow L$ $H - 1 \rightarrow L + 1$
	S_2	27 747 (3.44)	0.0000	$H \rightarrow L + 1$ $H - 1 \rightarrow L$
A,D	S_1	27 028 (3.35)		$H \rightarrow L + 1$ $H - 1 \rightarrow L$
	S_2	28 101 (3.48)		$H \rightarrow L + 1$ $H - 1 \rightarrow L$
A−D	S_1	27 451 (3.40)	1.1252	$H \rightarrow L$ $H - 3 \rightarrow L + 3$
	S_2	28 075 (3.48)	0.0000	$H - 1 \rightarrow L + 2$ $H - 2 \rightarrow L + 1$
	S_3	28 780 (3.57)	3.1626	$H - 1 \rightarrow L + 1$ $H - 2 \rightarrow L + 2$
	S_4	28 901 (3.58)	0.0000	$H \rightarrow L + 3$ $H - 1 \rightarrow L + 2$ $H - 3 \rightarrow L$

[a] See Figure 5 for nomenclature. [b] Oscillator strength. [c] H for HOMO (highest occupied molecular orbital) and L for LUMO (lowest unoccupied molecular orbital).

According to Figure 5, two main intermolecular interactions may exist in the subcrystalline form: the dimer formed by molecules A and B, which are parallel, and the dimer formed by molecules A and D. The dimer A,C (results not shown) has also been considered, but the electronic properties were found quasi similar to that of the dimer A,D. Figure 6 shows that the

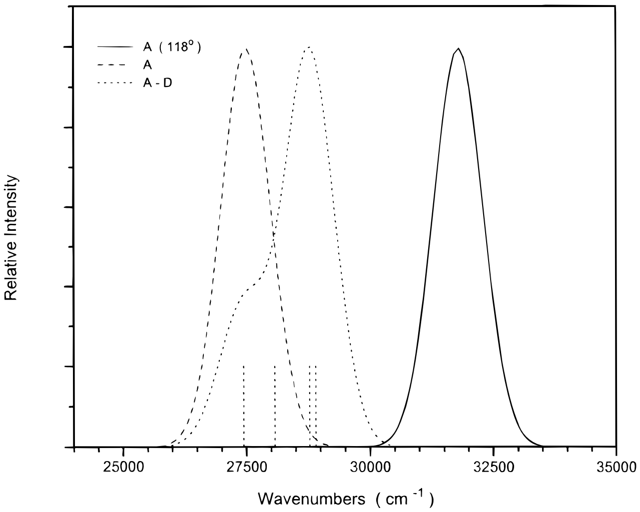

Figure 7. Simulated absorption spectra of DMTT. Letters in the legend represent the DMTT molecules (see Figure 5) involved in the crystalline form calculated. The spectrum of the free molecule (118°) is obtained as discussed in the text. The normalized transition energies of the tetramer are also indicated.

interaction between molecules A and B does not significantly affect the energy of the S_1 excited singlet state of the isolated molecule. This is explained by the small overlapping between molecules A and B, which gives weak intermolecular interactions. However, the energies of the triplet states are more affected by the interactions involved in the dimer A,B. Indeed, one can notice a convergence of the triplet states as observed for the TT aggregates. On the other hand, the interaction between molecules A and D induces a small excitonic splitting of the S_1 excited singlet state. The $S_1 \leftarrow S_0$ electronic transition of the dimer A,D appears at a slightly smaller energy than that of the single molecule and is less intense whereas the $S_2 \leftarrow S_0$ electronic transition is blue shifted and is very intense. It is important to point out that the blue shift observed for the second electronic transition (611 cm^{-1}) compared to that of the single molecule is smaller than that found for the dimer A,B of TT (953 cm^{-1}).

For the tetramer, the $S_1 \leftarrow S_0$ electronic transition appears at about the same energy than that of the isolated molecule and is quite intense ($f = 1.1252$). But the most allowed singlet−singlet transition corresponds to the $S_3 \leftarrow S_0$ transition, which is blue shifted by 1290 cm^{-1} compared to that of the isolated molecule. The value of this shift is much smaller than that induced by the intermolecular interactions occurring for TT (2513 cm^{-1}). Moreover the red shift of the first allowed singlet transition between the free and isolated molecules caused by the packing effect present in the solid phase of DMTT (4296 cm^{-1} calculated and 2250 cm^{-1} measured; see above) is much larger than the blue shift of the singlet transition between the isolated and aggregated form induced by intermolecular interactions.

The simulated absorption spectra of DMTT using the crystalline structure and possessing dihedral angle values of 30° (in the solid state) and 118° (in solution) are displayed in Figure 7. One can see that the packing effect present for DMTT, for an isolated molecule, in the solid state induces a very large red shift of its absorption band. But, as mentioned above, the energy difference between the $S_1 \leftarrow S_0$ electronic transition of these two conformations could be overestimated by ZINDO/S calculations. On the other hand, the simulated absorption spectrum of the tetramer shows a component at about the same energy as that observed for the isolated molecule in the solid state, but the more intense peak is blue shifted (see Figure 7 and Table 3). The spectral properties shown here for DMTT are quite different from those reported above for TT. Indeed, the main band of the tetramer located at 28 780 cm^{-1} is red shifted compared to the absorption band of DMTT in solution ($\theta = 118°$). These theoretical results are in good agreement with the experimental results shown in part 1 of this series of papers[39] (see Figure 9B). Indeed, following the aggregation process, the excitation spectrum of DMTT is red shifted compared to the absorption spectrum recorded in solution. It is worth mentioning here that the excitonic splitting calculated for clusters retaining the perfect crystalline geometry is certainly maximized compared to real life. One expects that for aggregated forms or solid states (evaporated solution of DMTT),[39] the actual splitting is less. Moreover, compared with the excitation spectrum of DMTT molecules isolated in an alkane matrix at 77 K, the

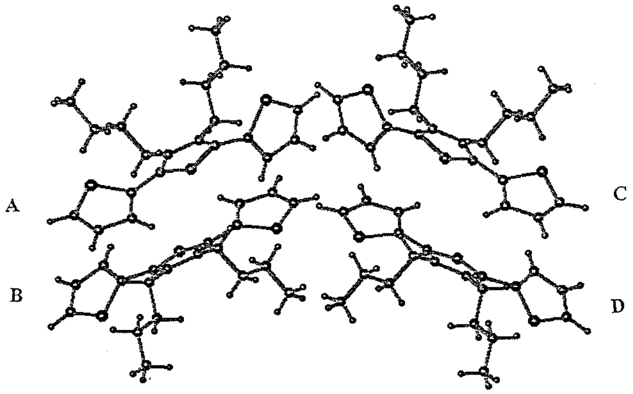

Figure 8. Crystalline structure of DBTT. The labels (A−D) are used to identify each molecule in the subcrystalline structures used for the ZINDO/S calculations.

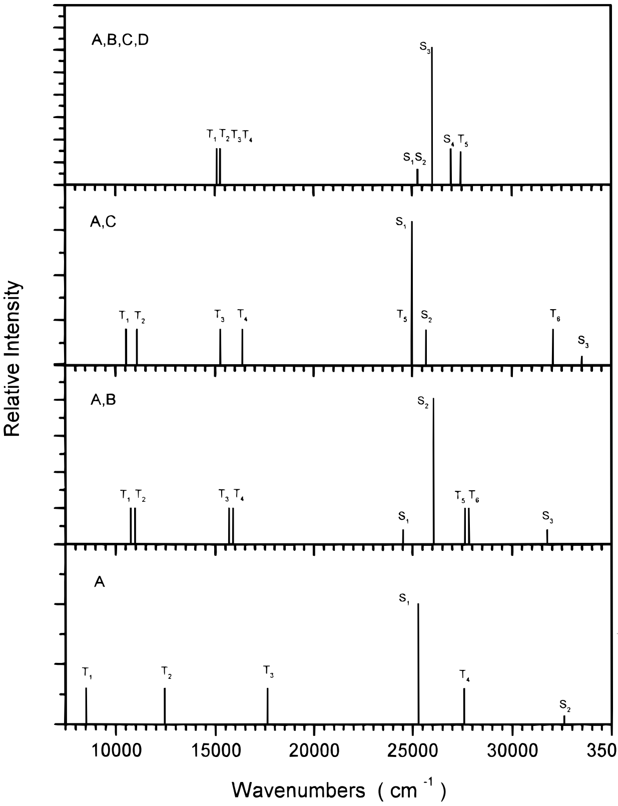

Figure 9. Calculated singlet−singlet and singlet−triplet electronic transitions of DBTT. The intensities of the forbidden (or weakly allowed) transitions are increased arbitrarily to be visible. Letters on each window represent the DBTT molecules (see Figure 8) involved in the crystalline form investigated (from 1 to 4 molecules).

TABLE 4: Energy (Relative to the S_0 State), Oscillator Strength, and Molecular Orbitals (MO) Involved for First Excited Singlet States of Subcrystalline Forms of DBTT

subcrystalline forms[a]	excited singlet states	energy [cm^{-1} (eV)]	f[b]	MO[c]
A	S_1	25 265 (3.13)	1.0039	H → L
A,B	S_1	24 504 (3.04)	0.0050	H → L + 1 H − 1 → L
	S_2	26 042 (3.23)	2.0206	H → L H − 1 → L + 1
A,C	S_1	24 969 (3.10)	1.5934	H → L + 1 H − 1 → L
	S_2	25 680 (3.18)	0.3931	H → L + 1 H − 1 → L + 1
A−D	S_1	25 259 (3.13)	0.0100	H − 1 → L + 2
	S_2	25 265 (3.13)	0.0213	H → L + 3 H − 2 → L + 1
	S_3	26 001 (3.22)	3.0508	
	S_4	27 427 (3.40)	0.7306	

[a] See Figure 8 for nomenclature. [b] Oscillator strength. [c] H for HOMO (highest occupied molecular orbital) and L for LUMO (lowest unoccupied molecular orbital).

excitation spectrum of the aggregated forms shows a first band close to the 0,0 vibronic peak (~25 100 cm^{-1}). However, the intensity of this peak is weak compared to the rest of the absorption band. The main excitation peak of the aggregated forms appears near 28 200 cm^{-1}, which is blue shifted compared to the maximum of the excitation spectrum of the single molecule in the alkane matrix but is red shifted compared with the absorption band of DMTT in solution. The shift between the maximum of the excitation spectra of DMTT in the matrix and in the aggregated forms is ~1000 cm^{-1} (see Table 2), which is close to the value of 1290 cm^{-1} calculated between the maximum of the simulated spectra of the molecule isolated in the crystal and that of the tetramer. Obviously, the lack of resolution in the excitation spectra does not preclude the existence of different types of aggregates, which would cause an increase of the bandwidths, making the correlation with theoretical results more qualitative than quantitative.

3.3. 3′,4′-Dibutyl-2,2′:5′,2″-terthiophene (DBTT). The crystalline structure of a unit cell of DBTT[43] is shown in Figure 8. The four molecules are positioned such that no crystal plane is observed. Moreover molecules A and B (or C and D) are nearly perpendicular to each other. The thiophene backbones do not adopt a totally planar conformation but possess a dihedral angle $\theta \sim 30°$ from planarity whereas adjacent thiophene rings have an *anti-gauche* conformation. However, the molecular conformation in the crystal is more planar than the minimum energy conformation optimized for 3′,4′-diethyl-2,2′:5′,2″-terthiophene (DETT) using the HF/3-21G* ab initio method[40] as observed for TT and DMTT. Indeed, this lowest energy conformer has a dihedral angle $\theta = 105°$ due to the high steric effect caused by the presence of the alkyl groups. The increase in planarity of DBTT in the solid state is caused by the packing effect present in the crystal.

The electronic spectrum of a single molecule is shown in Figure 9, and the spectral characteristics are reported in Table 4. Experimental and calculated parameters are compared in Table 2. As observed for TT and DMTT, the $S_1 \leftarrow S_0$ electronic transition is allowed and appears at 25 265 cm^{-1} with an oscillator strength of 1.0039. This singlet−singlet transition is blue shifted compared to that of TT, due to the increase of the twisting angles in DBTT, but is red shifted compared to that of DMTT. This difference between DMTT and DBTT might be caused by the respective conformation adopted by the molecules (*anti* for DBTT and *anti-syn* for DMTT) and/or might involve the different positions of the substituents on the thiophene rings. The $S_1 \leftarrow S_0$ electronic transition of the isolated molecule having the crystalline structure but a dihedral angle $\theta = 105°$ (free) is located at 32 010 cm^{-1} with an oscillator strength of 0.564. As expected, this transition is blue shifted and the oscillator strength is reduced. The energetic difference between the $S_1 \leftarrow S_0$ transitions involving these two conformations is calculated to be 6745 cm^{-1} (see Table 2), which is much larger than that observed experimentally (2690 cm^{-1}; see Figure 5B or 10B of part 1 and Table 2 of this paper). As discussed above for DMTT, we believe that ZINDO/S calculations may overestimate the absolute energy of electronic transitions for much twisted conformers. As observed for TT, the comparison between experimental and calculated first allowed transitions (see Table 2) is good and inside the 2000 cm^{-1} bracket.

The first dimer considered in the cell unit involves molecules A and B. The electronic spectrum of the dimer A,B is displayed in Figure 9. One can see that the intermolecular interaction between these two molecules caused a Davydov splitting of the S_1 excited singlet state, giving rise to a weak $S_1 \leftarrow S_0$ transition which is red shifted (761 cm^{-1}) and a $S_2 \leftarrow S_0$ transition which is blue shifted (777 cm^{-1}) and more intense compared to the isolated molecule first electronic $S_0{-}S_1$ transition. These spectral shifts are smaller than those reported above for TT but slightly larger than those calculated for DMTT. This suggests that the interaction between two DBTT molecules in the solid state is slightly larger than the intermolecular interaction found for DMTT in the same environment. The second type of dimer investigated involving molecules A and C does not show any significant excitonic effect indicating that the intermolecular interaction between these two molecules is weak.

Contrary to the dimer A,B, the first singlet−singlet transition of the tetramer A,B,C,D is located at the same wavelength as that calculated for the isolated molecule (see Figure 9). This behavior is similar to the one discussed above for TT where the S_1 state of the tetramer was not as red shifted as that of the dimer. On the other hand, the most intense transition ($S_3 \leftarrow S_0$) of the tetramer is blue shifted, compared to the single molecule, by exactly the same amount than that calculated for the dimer ($S_2 \leftarrow S_0$). One can also observed that the $S_4 \leftarrow S_0$ transition is more intense and is blue shifted compared to the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ electronic transitions. As observed for DMTT, the most intense singlet−singlet transition is not as blue shifted (736 cm^{-1}) as that found for TT (2513 cm^{-1}). Moreover the blue shift observed is small compared to the red shift (6745 cm^{-1}) caused by the packing effect present in the solid state, which increases the planarity of the molecules.

The simulated spectra of the various species are shown in Figure 10. It is observed again that the absorption spectrum of the molecule isolated in the crystal and that of the tetramer are close to each other whereas the absorption band of the molecule in solution ($\theta = 105°$) is blue shifted. Once again, these theoretical results provide a good correlation with the experimental results reported in part 1 of this series of paper[39] (see Figure 10B) and in Table 2 of this paper.

Overall, it is observed that intermolecular interactions involving substituted terthiophenes lead to a smaller excitonic effect in the absorption spectra of these molecules than that found for TT. This clearly indicates that the addition of side groups to the main chromophore weakens the interaction between these molecules in the solid state. This is certainly due to the different arrangements found in the solid state for these oligothiophenes.

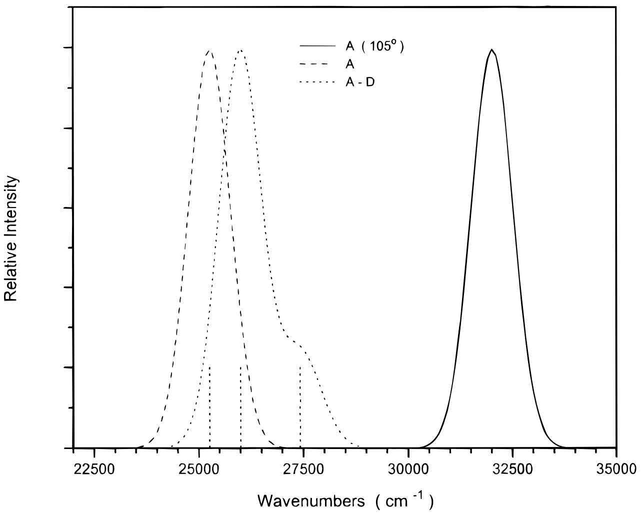

Figure 10. Simulated absorption spectra of DBTT. Letters in the legend represent the DBTT molecules (see Figure 8) involved in the crystalline form calculated. The spectrum of the free molecule (105°) is obtained as discussed in the text. The normalized transition energies of the tetramer are also indicated.

Indeed, the presence of the lateral side chains increases intermolecular distances and modifies the orientations, which should decrease the overlap between p_z orbitals of neighboring molecules. Moreover, the nonplanarity of the thiophene backbones in the crystals could also play a role in the decrease of the intermolecular interactions. To gain a better knowledge of the importance of the last point, ZINDO/S calculations performed on the crystallographic structure of 3,3″-dimethoxy-2,2′:5′,2″-terthiophene (DMOTT) would be helpful. Indeed, it was shown in part 1[39] that this molecule in solution is nearly planar such that no important conformational changes are expected to be induced by the packing effect in the solid state. On the other hand, in the solid state, the intermolecular interactions would be emphasized alone since being the only factors influencing the absorption spectrum. Moreover, the absorption spectrum of DMOTT in its aggregated form reported in part 1[39] does not show any excitonic splitting following aggregation. Unfortunately, X-ray data about DMOTT are still missing in the literature. To further investigate the influence of the molecular conformation on the intermolecular interactions, ZINDO/S calculations have been done for the crystalline structure of 3,3′-dimethoxy-2,2′-bithiophene.[50] These results, compared with those performed for the X-ray structure of BT,[51] do not show any important excitonic splitting despite the fact that this molecule is nearly planar.[25] ZINDO/S calculations[52] have also been performed on the crystalline structure of 3,3‴-dimethoxy-2,2′:5′,2″:5″,2‴-quaterthiophene (DMOQT).[53] Results show a weaker excitonic splitting on the first allowed singlet transition compared to that calculated for quaterthiophene (QT) despite the fact that the former molecule is nearly planar in the solid state. These results are in agreement with the experimental results. All these experimental and theoretical results indicate that the sole presence of lateral chains prevents the formation of a compact and ordered crystalline structure. Breaking off the highly ordered crystalline form is the principal cause of the weakness of the excitonic effect observed in substituted terthiophenes.

Both these papers (parts 1 and 2) have adressed the issue of the electronic excitations in aggregates with varying degrees of electronic intermolecular interactions using model compounds. A good understanding of the electronic excitation mechanism is required to bridge the gap between molecular electronics and device physics in the field of semiconducting polymers.

4. Concluding Remarks

It is shown in this paper that sandwich-type intermolecular interactions involve for unsubstituted terthiophene (TT) in its crystalline form induce an important excitonic splitting of its absorption spectrum. On the other hand, head-to-tail intermolecular interactions do not significantly affect the spectral properties of TT. The appearance of a weak red-shifted band and an intense blue-shifted band in the absorption spectrum of TT in its aggregated form is in good agreement with experimental results reported in part 1 of this study. The blue shift of the allowed transition increases with the number of molecules in interaction while the red shift of the weak band is reduced. Since TT is not much twisted in solution ($\theta = 150°$), the change of conformation of TT in the solid state caused by the packing effect is relatively weak such that the red shift resulting from the increase of molecular planarity is overcome by the blue shift induced by the formation of aggregates.

In contrast, the crystalline structure of alkyl-substituted terthiophenes is less ordered leading to weaker electronic interactions between neighboring molecules, giving rise to weaker excitonic effects. For these derivatives, the conformational changes occurring in the solid state are large such that the absorption red shift due to the increase of planarity emcompasses the blue shift resulting from intermolecular interactions present in the solid state. In other words, the chromic effects observed for alkyl-substituted terthiophenes are mainly due to conformational changes instead of excitonic splittings as observed for unsubstituted oligothiophenes.

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