UV–Vis, IR, Raman and theoretical characterization of a novel quinoid oligothiophene molecular material

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Received 3 September 2002; accepted 26 September 2002

Abstract

A quinoid-type oligothiophene, 3',4'-dibutyl-5,5'-bis(dicyanomethylene)-5,5'-dihydro-2,2',5',2''-terthiophene, which can be viewed as an analog of TCNQ, has been investigated by spectroelectrochemistry and density functional theory calculations, in its neutral and dianionic states. Electrochemical data show that the molecule can be both reduced and oxidized at relatively low potentials. Upon reduction, both experiments and theory agree well with the generation of a dianionic charged species. The model shows that the electronic structure of the dianion is consistent with two anionic dicyanomethylene groups attached to a central terthienyl spine having an aromatic structure. The two negatively charged dicyanomethylene groups conjugate with the terthiophene allowing for the extension of the \( p \)-delocalized system over the whole molecule. The stability of the dianionic species, due to its aromatic character, gives support to the low value for the electrochemical two-electron reduction process. Infrared spectra of the neutral and of the dianion species have been assigned and correlated.

Keywords: Oligothiophenes; Electrochemistry; Quinoid structure; Electronic spectra; Vibrational spectra; Theoretical calculations; Dianion

1. Introduction

The investigation of oligothiophenes bearing a quinoid structure has been the focus of a continuing intense research effort [1–3]. The demonstration that 3',4'-dibutyl-5,5'-bis(dicyanomethylene)-5,5'-dihydro-2,2',5',2''-terthiophene (Bu\textsubscript{2}(DCM)\textsubscript{2}Tth, Fig. 1) behaves as an \( n \)-channel conductor in a thin film transistor is somewhat outstanding since oligothiophenes are usually viewed as electron-rich molecules capable of \( p \)-type transport. Therefore the discovery of the \( n \)-channel and the amphoteric redox behavior of Bu\textsubscript{2}(DCM)\textsubscript{2}Tth suggests the possibility of obtaining organic-based materials with ambipolar character [1].

From a molecular point of view, ambipolar behavior for a given material is related with its capability of stabilizing negative and positive charges. The study of these charged species becomes, thus, an essential step for the design of materials with relevant electrical properties. Detailed structural and electronic information can be extracted by matching the analysis of
electronic and infrared spectra with quantum chemical models [4,5]. Difficulties in obtaining molecular structure data by using conventional experimental techniques (i.e. X-ray measurements, etc.), when charged or unstable species are studied, makes the combination of theory and molecular spectroscopy a powerful tool to get access to reliable molecular and electronic parameters. Organic molecules derived from thiophene give rise to solid materials in which weak Van der Waals and intermolecular interactions take place. Thus, the macroscopic or emerging properties of the material keep the identity of the molecular property. This characteristic supports the use of theoretical models dealing with isolated entities to understand solid-state properties.

In this work, we present spectroelectrochemical visible and infrared experiments performed on Bu$_2$(DCM)$_2$Tth. The data are supported and interpreted with the aid of sophisticated DFT quantum chemical calculations of both optimized geometries and infrared spectra.

2. Experimental and computational details

The synthesis and purification of Bu$_2$(DCM)$_2$Tth is described elsewhere [2]. Spectroelectrochemical measurements in the visible region were carried out in a 0.1 M tetrabutylammonium hexafluoroborate (TBABF$_6$)/CH$_2$Cl$_2$ solution with a 0.053 M concentration of Bu$_2$(DCM)$_2$Tth using an Ag/Ag$^+$ electrode as reference, a double ITO sheet as working electrode and a Pt wire as counterelectrode. Electronic spectra in the visible region (400–900 nm) were obtained with a Perkin–Elmer Lambda 19 spectrometer. Spectra in the IR region (2500–700 cm$^{-1}$) were obtained with a Nicolet 550 IR spectrometer equipped with a MCD detector as previously reported [2].

Density Functional Theory (DFT) calculations have been proved very attractive in computing molecular properties of many classes of $\pi$-delocalized systems since they implicitly account for electronic correlation although the computational cost is comparable to that of the Hartree–Fock calculations [6–8]. Theoretical calculations including geometry optimizations and infrared spectra were carried out at the DFT level using the Becke’s three-parameter B3LYP exchange-correlation functional [9] and the 6-31G** basis set [10]. The calculated harmonic vibrational frequencies were scaled down by a factor of 0.96 as recommended by Scott and Radom [11]. All the calculations were performed using the A.7 revision of the gaussian 98 program package [12] running on SGI Origin 2000 computers and IBM RS/6000 workstations.

3. Optimized geometries and charges

Fig. 2 displays the B3LYP/6-31G** optimized bond lengths and the Mulliken net atomic charges for the neutral and for the dianionic species of Bu$_2$(DCM)$_2$Tth. The neutral molecule exhibits a heteroquinoid structure in which the three thiophene rings and the dicyano-methylene groups are coplanar with the exception of the two butyl groups. According to the DFT/B3LYP/6-31G** calculations, the incorporation of two electrons induces important changes in the structure of the molecule. The terthiienyl backbone changes from a quinoid to an aromatic structure which is more pronounced in the central ring than in the two outermost ones. This can be likely due to (a) the conjugative effects from the two charged dicyano-methylene groups towards the two closest thiophene rings, and (b) the slight distortion from coplanarity of the dianion with respect to the neutral system (the dihedral S–C–C–S angle, defined by the central and the end rings, is 146.1° in the dianion versus 180° in the neutral molecule). The C–C–N bonds in the dianion are slightly lengthened with respect to those of the neutral system, whereas the C–CN bonds are shortened by ca. 0.014 Å upon reduction. The decrease of the bond alternation pattern in these dicyano-methylene groups agrees with the aforementioned extension of the conjugation from the end...
charged C(CN)$_2$ groups to the central terthiophene moiety.

The analysis of the B3LYP/6-31G** charges reveals that the excess of charge in the dianion is mainly localized over the outer dicyano-methylene groups, and agrees with their strong deficient character (i.e. they bear ca. $-0.3e$ even in the neutral species). It is noteworthy that in the neutral state the central thiophene ring significantly resents the electron extracting effects by the end two dicyano-methylene groups (i.e. its overall charge changes from $+0.11$ to $-0.08e$ from the neutral to the dianion).

4. Electronic spectra

Fig. 3 shows the absorption electronic spectra of the neutral molecule and of the electrochemically reduced Bu$_2$(DCM)$_2$Tth. The neutral molecule displays an intense electronic feature at 670 nm that corresponds to the $\pi - \pi^*$ transition and two shoulders at the high (625 nm) and the low (710 nm) energy side of the intense band. The latter arise from 0–0 vibronic transition due to the rigidified structure. The reduction

Fig. 3. Visible absorption electronic spectra of (a) neutral Bu$_2$(DCM)$_2$Tth and (b) electrochemically doubly charged Bu$_2$(DCM)$_2$Tth.
induces the disappearance of the intense band of the neutral molecule and the emergence of a weak-medium intensity band at 451 nm. The wavelength for the new species is in the range of that of the common aromatic oligothiophenes [13]. An intermediate species corresponding to a generation of a mono-anion radical has also been described [2] for Bu₂(DCM)₂Tth but is not discussed in the context of this paper.

5. Infrared spectrum of the neutral Bu₂(DCM)₂Tth

Fig. 4 displays the experimental and theoretical B3LYP/6-31G** infrared spectra of Bu₂(DCM)₂Tth in the 2500–700 cm⁻¹ spectral region. The experimental spectrum corresponds to that recorded in situ as a function of applied potential. The ν(C≡N) vibration for the neutral molecule is measured at 2211 cm⁻¹ in the experimental infrared spectrum with a shoulder at 2182 cm⁻¹. These two bands can be correlated with the A and B ν(C≡N) modes, respectively, calculated at 2239 and 2220 cm⁻¹. The splitting of the ν(C≡N) vibrations (appearance of the A and B modes) is consistent with a significant coupling between the four CN groups due to the rigidity of the molecule. The extension of the π-electron delocalization over the entire molecule is supported by the Raman spectrum in which the ν(C≡N) vibration band appears as a very intense feature at 2208 cm⁻¹. The selectively enhancement of this Raman band among the very many Raman-active vibrations of the molecule clearly shows the large participation of the cyano groups in the π→π⁺ chromophore.

The peak position of the infrared ν(C≡N) vibration at 2211 cm⁻¹ is useful for estimating the degree of intramolecular charge transfer since it is highly sensitive to the electron density of the CN triple bond. This band largely downshifts on complexation with electron-donors or after reduction [2,3,14,15]. For example, the infrared ν(C≡N) band of neutral TCNQ appears at 2225 ± 5 cm⁻¹, at 2197 cm⁻¹ for TCNQ⁻ and at 2164 cm⁻¹ for TCNQ²⁻ [14,16–19]. In similar molecules, the ν(C≡N) frequency peak appears at 2211 cm⁻¹ in the solid β-trishexyl (DCM)₂Tth, at 2210 cm⁻¹ in (DCM)₂Tth or at 2206 cm⁻¹ in β-tetrahexyl (DCM)₂Qth (Q = quaterthiophene) [3]. According to Fig. 1 in Ref. [20], the intramolecular charge transfer can be...
estimated to be approximately $\rho = 0.4$ for neutral Bu$_2$(DCM)$_2$Tth.

A large resemblance between theory and experiment is observed in the whole spectral range. The $C_2$ symmetry assumed in the calculations agrees quite well with the experimental data obtained in solution, and thus conformational distortions from coplanarity are expected to be negligible. In the medium frequency range, the band at 1517 cm$^{-1}$ can be correlated with the theoretical band at 1510 cm$^{-1}$. According to its eigenvector (Fig. 5), the vibration corresponds to an antisymmetric stretching vibration of the C$_{\beta}$=C$_{\beta}$ bonds mainly located on the outermost rings. The band at 1468 cm$^{-1}$ correlates with the strongest theoretical IR band at 1460 cm$^{-1}$. This band can be described as an antisymmetric stretching vibration of the C$_{\alpha}$=C$_{sp2}$ bonds somewhat coupled with the inter-ring C=C and with the central C$_{\beta}$=C$_{\beta}$ stretching vibration.

Bands at 1284 and at 1241 cm$^{-1}$ can be assigned to the antisymmetric in-plane C–H deformation vibrations, $\delta$(C–H), coupled with $\delta$(CH$_2$) and $\delta$(CH$_3$) modes. See for instance the eigenvector associated to the theoretical band at 1231 cm$^{-1}$.

Fig. 5. B3LYP/6-31G** eigenvectors calculated for selected vibrations of the theoretical infrared spectrum of the neutral Bu$_2$(DCM)$_2$Tth. Values correspond to scaled wavenumbers in cm$^{-1}$. 

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$\rho$, $\delta$, $\beta$, $\alpha$, $C_{\alpha}$, $C_{sp2}$, $C_{\beta}$, $C_{\beta}$
which compares with the experimental one at 1241 cm\(^{-1}\). The band at 1181 cm\(^{-1}\), calculated at 1164 cm\(^{-1}\), can be described as a C–C stretching vibration coupled to some extent with \(\nu(C=C)\) and \(\delta(C–H)\) modes (Fig. 5).

The electronic structure of neutral \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) can be related with that of the dicationic species generated in aromatic oligothiophenes. In particular, the comparison of the infrared spectra of \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) and that of the dicationic species of \(\alpha,\alpha’\)-diphenyl tetrabutyl sexithiophene (\(\text{Bu}_4\text{Ph}_2\text{SxT}^{+2}\)) reveals interesting similarities[5]. The infrared spectrum of \(\text{Bu}_4\text{Ph}_2\text{SxT}^{+2}\) displays one very strong band at 1365 cm\(^{-1}\) together with minor absorptions at 1401, 1222 and 1180 cm\(^{-1}\) whose whole appearance can be roughly correlated with infrared spectral pattern of \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) consisting on one very strong band at 1468 cm\(^{-1}\) while the rest of the spectrum consists on medium and weak features. Although the dynamic of \(\text{Bu}_4\text{Ph}_2\text{SxT}^{+2}\) is different to that of \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) the resemblance between these two spectra invokes that \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) can be used as a model of the dication in oxidized oligothiophenes and of the bipolaron in doped polythiophene.

6. Infrared spectra of the dianion species of \(\text{Bu}_2(\text{DCM})_2\text{Tth}\)

Fig. 6 displays the infrared spectrum of the electrochemically doubly reduced species of \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) together with the B3LYP/6-31G** theoretical infrared spectrum of the model dianion (\(\text{Bu}_2(\text{DCM})_2\text{Tth}^{2-}\)). Fig. 7 depicts the eigenvectors associated to the most important infrared bands of \(\text{Bu}_2(\text{DCM})_2\text{Tth}^{2-}\). Excellent accordance between experimental and theoretical features is found. This comparison does support the existence of dianionic species in \(\text{Bu}_2(\text{DCM})_2\text{Tth}\) upon electrochemical double charging of the neutral molecule.

The band due to the \(\nu(C≡N)\) stretching vibration in the neutral system splits upon reduction. The two intense bands experimentally measured at 2166 and at 2114 cm\(^{-1}\) can be correlated with the theoretical features at 2186 and at 2153 cm\(^{-1}\). Although calculation somewhat overestimates the experimental values, the difference between the wavenumber value for the \(\nu(C≡N)\) band in the neutral molecule and for that of the higher \(\nu(C≡N)\) band in the dianion, 45 cm\(^{-1}\), is accurately reproduced by the theoretical
The higher wavenumber band can be described as an antisymmetric stretching vibration of the four CN bonds. On the other hand, calculations reproduce the existence of two symmetric stretching vibrations of the four CN bonds at 2153 cm\(^{-1}\) (2153.7 and 2153.5 cm\(^{-1}\)) which can correlate, respectively, with the experimental bands at 2125 cm\(^{-1}\), which is a shoulder, and with the band at 2114 cm\(^{-1}\). We have to remark that these modes are not exclusive vibrations of the CN bonds but are extended over the whole dicyano-methylene groups as observed by the coupling with the C–CN stretching vibrations.

The medium energy region of the infrared spectrum of the double reduced species of Bu\(_2\)(DCM)\(_2\)Th is dominated by the presence of two main bands at 1504 and 1456 cm\(^{-1}\). These bands correlate with those calculated at 1483 and 1440 cm\(^{-1}\) in Bu\(_2\)(DCM)\(_2\)Th\(^{-2}\) (Fig. 7 for the schematic B3LYP/6-31G** eigenvectors). The theoretical vibration at 1483 cm\(^{-1}\) can be mainly

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Fig. 7. B3LYP/6-31G** eigenvectors calculated for selected vibrations of the theoretical infrared spectrum of the dianionic species of Bu\(_2\)(DCM)\(_2\)Th. Values correspond to scaled wavenumbers in cm\(^{-1}\).
described as an antisymmetric stretching vibration of the C=C bond, \( \nu_6(C= C) \), of the thiophene rings. As shown by the corresponding eigenvectors, this vibration can be correlated with the experimental feature of the neutral molecule at 1354 cm\(^{-1}\) and calculated at 1352 cm\(^{-1}\). The upshift from 1354 to 1504 cm\(^{-1}\) upon reduction is in agreement with the strengthening of these CC bonds due to the aromatization of the molecule. In this regard, we have studied a series of neutral \( \alpha,\alpha' \)-dimethyl aromatic oligothiophenes from a dimer to an hexamer for which this \( \nu_6(C= C) \) mode in the infrared spectrum appears at 1531 cm\(^{-1}\) in the \( \alpha,\alpha' \)-dimethylbi thiophene, at 1518 cm\(^{-1}\) in the \( \alpha,\alpha' \)-dimethyler thiophene, at 1513 cm\(^{-1}\) in \( \alpha,\alpha' \)-dim ethylquater thiophene, at 1508 cm\(^{-1}\) in the \( \alpha,\alpha' \)-dimethylpentathiophene and at 1503 cm\(^{-1}\) in the \( \alpha,\alpha' \)-dimethylsexithiophene [21]. Therefore, the \( \nu_6(C= C) \) band wavenumber of \( \text{Bu}_2(DCM)_2\text{Tth} \) correlates with that of a neutral pentamer or hexamer that is in agreement with the extension of the conjugation to the terminal dicyano-methylene groups.

The theoretical band at 1440 cm\(^{-1}\), experimentally measured at 1456 cm\(^{-1}\), is the most intense feature of both spectra and can be described as a deformation vibration of the CH\(_2\) and CH\(_3\) groups of the two butyl groups. The existence of up to eight oscillators can justify its large intensity. This band correlates with that at 1468 cm\(^{-1}\) in the infrared spectrum of the neutral molecule and the downshift by 12 cm\(^{-1}\) is justified by the involvement in this mode of the CC inter-ring stretching vibrations.

The weak intensity band at 1340 cm\(^{-1}\) must be related with the B3LYP/6-31G** feature calculated at 1331 cm\(^{-1}\). Its eigenvector (Fig. 7) shows that it corresponds to an antisymmetric C\(_6\)H\(_6\) stretching vibration of the thiophene rings. This band is related with that measured at 1517 cm\(^{-1}\) in the neutral molecule (1510 cm\(^{-1}\) in the theoretical spectrum) while the downshift by 177 cm\(^{-1}\) from the neutral to the double charge species is amounted by the lack of double bond character upon reduction and consequent aromatization.

Finally, the analysis of the eigenvector associated to the theoretical band at 1042 cm\(^{-1}\), experimentally measured at 1060 cm\(^{-1}\), indicates that its vibration mainly consists on a symmetric deformation vibration of the thiényl C–H bonds coupled with the \( \delta(CH_2) \) and with the \( \pi(C-C) \) modes.

### 7. Conclusions

We have assigned and correlated the main infrared bands of the neutral and the electrochemically doubly charged species of \( \text{Bu}_2(DCM)_2\text{Tth} \) with the aid of theoretical calculations carried out with the DFT methodology at the B3LYP/6-31G** level. Excellent agreement is obtained between the infrared spectrum of the doubly charged species of \( \text{Bu}_2(DCM)_2\text{Tth} \) and of the theoretical infrared spectrum of \( \text{Bu}_2(DCM)_2\text{Tth}^{-2} \). The structure of \( \text{Bu}_2(DCM)_2\text{Tth}^{-2} \) can be described as an almost planar molecule in which the central terthiophene backbone displays an aromatic electronic structure and the two negative charges are mainly located on the dicyano-methylene groups due to their electron-negative character.

### Acknowledgements

The present work was supported by the Ministerio de Ciencia y Tecnología de Spain through the research projects BQU2000-1156 and PB98-1447. The group at the University of Málaga is indebted to the Junta de Andalucía for funding (FQM-0159). The group at the University of Valencia acknowledges the Generalitat Valenciana for a grant (GR01-145). J.C. is grateful to the Ministerio de Educación y Cultura of Spain for a postdoctoral fellowship (PF00-25327895).

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