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Intervalence Transitions in Mixed Valence Bis(tetrathiafulvalene) Compounds

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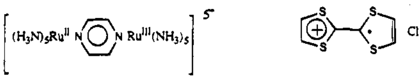
Abstract: The series of new bis(tetrathiafulvalene) [bis(TTF)] compounds **10−12a,b** have been synthetized with the TTF-like synthon **8a,b**, previously used to prepare the pyrazine-fused bis(TTF) **7a,b**. These compounds exhibit four reversible sequential one-electron oxidation steps, on the basis of cyclic voltammetry. For the cation radicals $\mathbf{7b}^{\bullet+}$, $\mathbf{10}^{\bullet+}$, and $\mathbf{12}^{\bullet+}$, generated electrochemically, rather intense and broad bands in the near-IR region, specific of class II mixed valence compounds, were found. Theoretical calculations at the semiempirical AM1 level as well as at the ab-initio level indicated that these cation radicals are charge-distributions localized as related to mixed valence species. These calculations also allowed the low-energy absorption bands to be assigned to intervalence transitions; these transitions imply the existence of multiple low-lying excited states that are non-adiabatically coupled to the ground-state of these open-shell species.

Introduction

Mixed valence compounds associate two (or more) electronically communicating, differing by one oxidation unit, otherwise identical redox sites. Inorganic mixed valence (MV) compounds, i.e., binuclear complexes containing two transition metal ions in different oxidation states, connected by a bridging ligand, such as the seminal Creutz−Taube complex **1**,[2] have been extensively studied.[3] An impetus to this large number of studies, aside from the fundamental interest in problems related to electron transfer processes, was given by the existence of suitable models, worked out in an early preexisting theoretical background,[4] which allowed a rational discussion of the properties of these MV complexes. These properties depend strongly on the extent of the electronic interaction between the redox centers and range, in accordance with the common classification,[5] from small (or nonexisting) (class I), slight (class II), to strong interaction (class III); the latter category includes exclusively the completely delocalized molecules. One of the most sensitive and direct ways to probe such interactions is the intervalence transfer (IT) band,[4] usually found in the near-IR.

Chart 1



1 **2**

In the absence of a corresponding theoretical framework, studies on purely organic mixed valence compounds are emerging much more slowly. While class I noninteracting centers need not be considered here, and many fully delocalized organic MV compounds, such as $TTF^{\bullet+}$ **2** (TTF = tetrathiafulvalene) (Chart 1), probably belonging to class III[6] exist, the organic class II mixed valence molecules are, on the other hand, much less common. Few examples have been described with the electrophores communicating by either saturated links, such as the anion radical of the unconjugated bis(indanone) **3**[7] (the first studied organic MV compound)[6] and the cation radicals from the σ-linked bis(hydrazine) **4**,[8] or unsaturated links, such as the anion radicals of polyacene diquinones **5**, developed by Miller and co-workers,[9] the poly(alkylmethyl) anion radicals,[10] and the oxidized aromatic polyamines[11a] or the reduced halo-

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(1) (a) Université de Paris-Sud. (b) Laboratoire de Chimie de Coordination du CNRS. (c) CEMES-LOE, CNRS. (d) Institut de Chimie.

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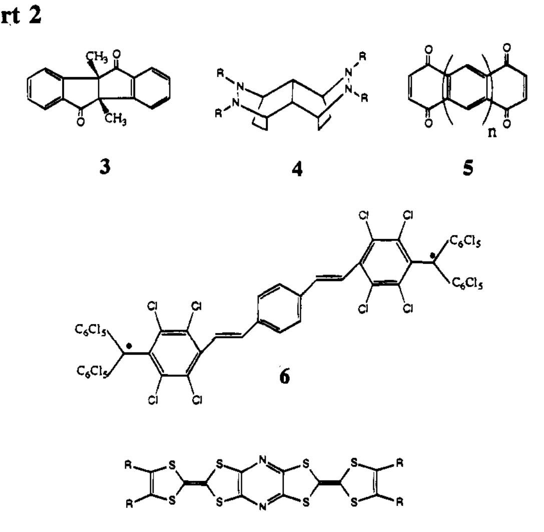
Chart 2



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7

genated diradicals **6**[11b] investigated by Bonvoisin et al. (Chart 2). These organic MV compounds exhibit interesting properties, reminiscent of their inorganic congeners, and similar intramolecular IT bands are observed, in the near-IR region. These absorption bands were discussed, also within the model developed by Hush,[4] in relation to the electronic interaction of the involved electrophores. Two limiting cases were identified, which were nicely illustrated in the series of Miller's semiquinones:[9] depending on the number of aryl rings between the electrophores, both *delocalized* ($\mathbf{5}^{\bullet-}$, $n = 1$) (Chart 2) (class III) and *localized* ($\mathbf{5}^{\bullet-}$, $n = 2, 3$) (class II) behavior was observed, although such π-electron localizations are unexpected for quinones connected by a planar conjugated π-system. However, difficulties were encountered[8a,11b] in applying, in this area, the model of Hush, due in part to the problem of defining the electrophores as clear single-charge centers, such as the metal ions in the inorganic MV complexes,[12] which is obviously not the case for organic compounds.

We have recently published[13] the synthesis of a new bis(TTF) compound, **7** (Chart 2). This so-called extended TTF,[14] containing two similar TTF electrophores connected by an aromatic link, exhibited four reversible sequential one-electron oxidation steps and could, a priori, if the cation radical therefrom is considered,[15] lead to mixed valence species, according to the above MV definition. We have presently extended this series of compounds to the bis(TTF) derivatives **10**–**12** (Figure 1), and report the corresponding synthesis and the solution electrochemical properties. We have generated electrochemically the corresponding cation radical of this series of bis(TTF) compounds, and report their optical properties in solution. In fact,we find that $\mathbf{7b}^{\bullet+}$, $\mathbf{10b}^{\bullet+}$, and $\mathbf{12b}^{\bullet+}$ exhibit intense and rather broad IT absorption bands in the near-IR, specific of (class II) mixed valence compounds. We have also performed theoretical calculations, at the semiempirical AM1 as well as ab-initio levels, and find that for these cation radicals, on the contrary to the parent delocalized $\mathrm{TTF}^{\bullet+}$, the *charge is unequally distributed* between the two electrophores; our calculations also point out mixed valence charge transfers involving these *localized* cation radical moieties, as usual electronic transitions, from the ground state to at least one nonadiabatically coupled low-lying excited state.

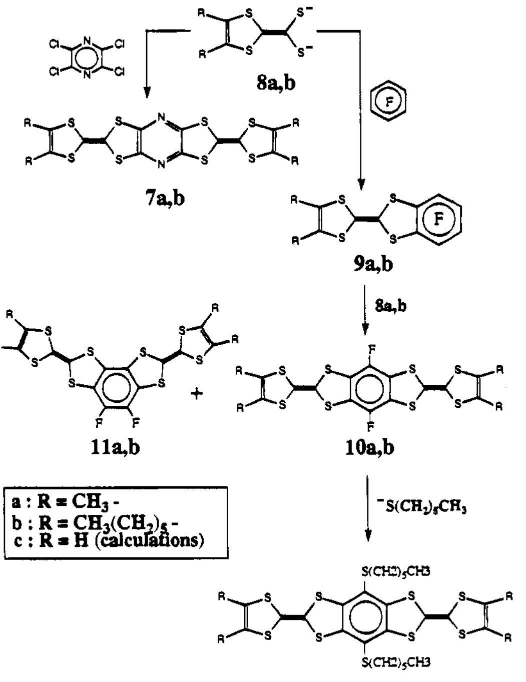

Figure 1. Synthetic scheme used to prepare the bis(TTF) compounds.

Experimental Section

The Synthesis and Electrochemical Studies of Compounds. General. Details of the instrumentation have been reported recently.[16] The procedures for the preparation of the nucleophiles **8a**,**b** as well as the synthesis of **7a**,**b** have been described previously.[13]

Nucleophilic Substitution by the Dilithium Salts 8a,b. General Procedure. The appropriate volume of the THF solution containing the salts **8a**,**b**[13] was syringed under argon into a vessel, and the THF evaporated under a rapid stream of argon. The residue was dissolved in oxygen-free DMF, and the required amounts of the substrate to be substituted were added. The mixtures were stirred overnight at room temperature, and the solids, whenever formed, were filtered; the residues were poured into water and filtered. The compounds were purified by recrystallization, Soxhlet extraction, or flash chromatography. The following were obtained.

2-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-4,5,6,7-tetrafluoro-1,3-benzodithiole (9a). **9a** was obtained from an excess of **8a** (5 equiv) as compared to hexafluorobenzene as an orange solid (65% yield). Mp: 205-206 °C (from cyclohexane). NMR (δ_H, $CDCl_3$): 1.95 (s). NMR (δ_C, CS_2): 11.37, 98.82, 117.95, 120.47 (ethylenic carbons), 118.60, 118.97, (d, $^2J_{CCF} = 20$ Hz), 133.99, 136.39, 139.00, 141.35 (dd, $^1J_{CF} = 250$ Hz). Anal. Calcd for $C_{12}S_4H_6F_4$: C, 40.68; H, 1.69; F, 21.47; S, 36.16. Found : C, 40.78; H, 1.48; F, 20.44; S, 36.20. MS (CI): *m/e* 355 (MH^+).

2-(4,5-Dihexyl-1,3-dithiol-2-ylidene)-4,5,6,7-tetrafluoro-1,3-benzodithiole (9b). **9b** was obtained from an excess of hexafluorobenzene (2 equiv) as compared to **8b** and isolated as an oil (60%) by flash chromatography eluting with cyclohexane. Anal. Calcd for $C_{22}H_{26}S_4F_4$: C, 53.44; H, 5.26; F, 15.38; S, 25.91. Found: C, 53.67; H, 5.37; F, 15.72; S, 26.01. MS (CI): *m/e* 495 (MH^+).

2,6-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,8-difluorobenzo[1,2-*d*:4,5-*d'*] bis[1,3]dithiole (10a) and 2,5-Bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-7,8-difluorobenzo[1,2-*d*:3,4-*d'*]bis[1,3]dithiole (11a). An

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excess of **9a** (4 equiv) was used as compared to **8a**; the solid formed was filtered and extracted by hot toluene, yielding **11a** as an orange solid (10%) (recrystallized from toluene). NMR (δ_H, CS_2): 1.95 (s). NMR (δ_C, CS_2): 14.1, 103.1, 119.8, 123.2 (ethylenic carbons), 124.5 125.8, (d, $^2J_{CCF} = 16$ Hz), 142.7 (dd, $^1J_{CF} = 254$ Hz, $^2J_{CCF} = 13$ Hz). Anal. Calcd. for $C_{18}H_{12}S_8F_2$: C, 41.38; H, 2.23; F, 7.28; S, 49.04. Found: C, 42.01; H, 2.27; F, 7.51; S, 48.48. MS (CI): *m/e* 523 (MH^+).

The insoluble part of this precipitate was then Soxhlet-extracted in toluene, yielding **10a** as an orange solid (40%). Anal. Calcd. for $C_{18}H_{12}S_8F_2$: C, 41.38; H, 2.23; F, 7.28; S, 49.04. Found: C, 41.01; H, 2.23; F, 7.64; S, 48.7. MS (CI): *m/e* 523 (MH^+).

2,6-Bis(4,5-dihexyl-1,3-dithiol-2-ylidene)-4,8-difluorobenzo[1,2-*d*:4,5-*d'*] bis[1,3]dithiole (10b) and 2,5-Bis(4,5-dihexyl-1,3-dithiol-2-ylidene)-7,8-difluorobenzo[1,2-*d*:3,4-*d'*]bis[1,3]dithiole (11b). A stoichiometric amount of **8b** was used as compared to **9b**; the solid formed in the reaction medium was filtered, and **10b**, an orange solid (31% yield), mp 210−212 °C, was isolated therefrom by recrystallization (dichromethane) (the same compound was obtained, although in lower overall yield (10%), in a one-step reaction from a 2:1 mixture of **8b** and hexafluorobenzene). NMR (δ_C, CS_2) : 14.95−31.34 (alkyl carbons), 103.49, 119.12, 129.05 (ethylenic carbons), 124.40 (d, $^2J_{CCF} = 10$ Hz), 145.63, (d, $^1J_{CF} = 245$ Hz). Anal. Calcd for $C_{38}H_{52}S_8F_2$: C, 56.85; H, 6.48; F, 4.73; S, 31.92. Found: C, 56.43; H, 5.94; F, 5.12; S, 32.01. MS (CI): *m/e* 802 (M^+).

The filtrate remaining after isolation of **10b** was evaporated to dryness, and the residue fractionated by flash chromatography eluting with cyclohexane yielded **11b** (5%) as a viscous orange oil, with the same R_f as **10b**. NMR (δ_C, CS_2): 14.84−32.29 (alkyl carbons), 101.93, 120.24, 128.95, 129.08 (ethylenic carbons), 121.9, 130.13 (d, $^2J_{CCF} = 18$ Hz), 141.42, (dd, $^1J_{CF} = 250$ Hz). MS (CI): *m/e* 802 (M^+).

4,8-Bis(1-hexylthio)-2,6-bis(4,5-dimethyl-1,3-dithiol-2-ylidene)-benzo[1,2-*d*:4,5-*d'*]bis[1,3]dithiole (12a) and 4,8-Bis(1-hexylthio)-2,6-bis(4,5-dihexyl-1,3-dithiol-2-ylidene)benzo[1,2-*d*:4,5-*d'*]bis[1,3]dithiole (12b). General Procedure. The lithium salt of 1-hexanethiol was generated in ether, using *n*-butyllithium (2.5 M in hexane), the solvents were evaporated, and the resulting solid was added (2:1 stoeichiometry) to **10a,b** in oxygen-free DMF. The mixtures were stirred overnight at 80 °C, and poured into water. The orange precipitates were filtered and purified by recrystallization from cyclohexane. The following were obtained: **12a**, (78%). Mp: 279−280 °C. NMR (δ_C, $CDCl_3$): 12.9−33.9 (alkyls), 103.2, 112.6, 121.9 (ethylenic carbons), 119.2, 142.0 (aromatic). Anal. Calcd for $C_{30}H_{38}S_{10}$: C, 50.14; H, 5.29; S, 44.57. Found: C, 50.03; H, 5.46; S, 44.49. MS (CI): *m/e* 718 (M^+). **12b** (80%). Mp: 184−185 °C. Anal. Calcd for $C_{50}H_{78}S_{10}$: C, 60.12; H, 7.81; S, 32.06. Found: C, 60.13; H, 7.88; S, 31.84.

Electrochemical Studies. Cyclic voltammetry was carried out with an Electro Kemat potentiostat using an interfacing hardware with a PC-compatible microcomputer.[17] The experiments were performed in an air-tight three-electrode cell connected to a vacuum/argon line in degassed anhydrous CH_2Cl_2 containing the substrates ($(0.4-0.8) \times 10^{-3}$ M), with added nBu_4NPF_6 (0.1 M). The reference electrode was a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counterelectrode was a platinum wire, and the working electrode a 2 mm diameter platinum rotating disk electrode (Tacussel EDI). Coulometric experiments were performed at room temperature on a platinum electrode with a large surface area (*ca.* 15 cm^2) at potentials slightly more positive than the needed half-wave oxidation potential. After the consumption of one electron for every considered oxidation step, the generated oxidized species were syringed for the optical spectroscopic and ESR studies.

Near-IR Spectroscopy. Absorption spectra were recorded with a Shimadzu UV-3101 PC Spectrophotometer.

ESR Spectroscopy. The ESR spectra of the dichloromethane solutions of the electrochemically generated oxidized species were recorded, at room temperature, using a Brucker ESP 300E intrument, equipped with a Brucker B-NM 20 gaussmeter and a EIP 548 microwave frequency counter, operating at X-band frequencies.

Calculations. Full geometry optimization, without symmetry restraint was performed for TTF, $TTF^{\bullet+}$, and for the bis(TTF) compounds **7c**, **10c**, and **11c** (Figure 1), at the ab-initio SCF level within the MINI-1′ [18,19] basis set within respectively restricted and unrestricted frameworks for the closed-shell species, the cation radicals, and the dication $\mathbf{10c}^{2+}$; the same calculations were also made at the semiempirical AM1[20] level. Subsequently, a determination of excited electronic states was made for these $bis(TTF)^{\bullet+}$ optimized geometries, i.e., in the Franck−Condon approximation, at either the CIS[21] or the UHF-SCF level. The first method expands the excited-state wave function on single electronic excited configurations, using the UHF spin orbitals of the fundamental doublet state, and is therefore a rapid way to provide a qualitative description of the excited states. Moreover, it allows the excited-state oscillator strength to be computed since the related mathematical expression can be analytically derived in this framework where the same MOs are used for both electronic states. However, a better energy classification of electronic states is obtained when they are all calculated at the UHF-SCF level. Unhappily, in this case, the derivation of the oscillator strength becomes more complicated and is not implemented in the usual quantum chemistry programs. The post-SCF CISD level is unavailable for these systems due to their size.

The stability of the UHF-SCF wave function describing the fundamental cation radical electronic states was also checked.[22] Such stability calculations indicate whether or not the UHF-SCF level is suitable to describe the investigated electronic state, i.e.,whether or not this state is coupled with another one. The program used for these calculations was the Unix version of GAUSSIAN 92[23] that was adapted on the FPS522 EA in Liège, Belgium.

Results

(a) Syntheses of the Bis(TTF) Compounds and the Electrochemical Properties. We have recently described a new general synthetic access to the TTF nucleus, via TTF-like synthons **8a,b**.[16] This approach was first applied to the synthesis of the pyrazine-fused bis(TTF) compounds **7a,b** (Figure 1), obtained in a single step by the aromatic nucleophilic substitution of tetrachloropyrazine by the bidentate nucleophiles **8a,b**.

Several similar extended-TTF donors, the linkage of the TTF subunits also being achieved through an aromatic ring, have been prepared in recent years, by Müllen and co-workers,[14] but using well-established TTF-forming coupling methods.

We feel that the present methodology might allow a more easy access to a variety of such π-extented TTF systems, and we report here the syntheses of compounds **10a,b−12a,b** obtained by the nucleophilic aromatic substitutions of hexafluorobenzene by the nucleophiles **8a,b**.

The reactions of an excess (2−5 equiv) of **8a,b** with hexafluorobenzene, carried out in oxygen-free DMF at room temperature, led to the unsymmetrically substituted TTF compounds **9a,b** with good yields (60−65%). Subsequent substitutions of the latter (used this time in excess as compared to the nucleophiles **8a,b**) led to the linearly fused TTF compounds **10a,b** with still acceptable yields (40% for **10a** and 31% for **10b**). Interestingly, a small amount (10% yield) of the angularly substituted regioisomer **11a**, the precursor of the 3-fold symmetry fully-TTF-substituted ring,[24] was also isolated.[25] Starting

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Table 1. Cyclic Voltammetry of the Synthesized Bis(TTF) Compounds vs SCE in CH_2Cl_2 with 0.1 M nBu_4NPF_6 at a Platinum Electrode (Scan Speed = 100 mV/s)

compd no.	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)	$E^3_{1/2}$ (V)	$E^4_{1/2}$ (V)
7b	0.49	0.71	1.24	1.50
10b	0.54	0.70	1.18	1.38
11a	0.56	0.72	1.14	ads.
12a	0.39	0.61	1.07	1.23

Table 2. Spectroscopic Data for Cation Radicals and Dications from Compounds **7**, **10**, and **12**[a]

species	UV−Vis/near-IR $\lambda(\epsilon \times 10^3)$[b]
7b	232 (22.9), 289 (17.9) sh, 324 (29.6), 397 (4.1), 533 (10.0)
10b	230 (41.6), 276 (33.4), 320 (42.7), 392 (4.6) sh, 453 (1.4) sh
12a	238 (14.4), 261 (17.7), 312 (21.1) sh, 324 (21.6), 451 (5.1)
7b$^{\bullet+}$	318 (14.3), 416 (10.2), 462 (11.1), 540 (7.7), 650 (11.8), 1700 (5.5) sh, 2500 (12.0)
10b$^{\bullet+}$	278 (29.6), 416 (15.3) sh, 454 (17.0), 638 (7.3), 1660 (4.6)
12a$^{\bullet+}$	266 (16.2), 304 (13.9), 416 (6.8) sh, 464 (8.5), 550 (4.5) sh, 630 (3.2), 1740 (4.3)
7b^{2+}	420 (17.9), 450 (10.5), 530 (7.1)
10b^{2+}	272 (24.2), 428 (33.5), 680 (11.6)
12a^{2+}	298 (7.8), 428 (17.0), 698 (4.8)

[a] In dichloromethane. [b] λ in nm and ϵ in M^{-1} cm^{-1}.

then from **10a**,**b**, the remaining fluorines were easily substituted by $CH_3(CH_2)_5S^-$, leading to the fully-sulfur-substituted compounds **12a**,**b**.

The electrochemical properties of the bis(TTF) compounds **7a**,**b** and **10**−**12a**,**b** were investigated by cyclic voltammetry, and the results are summarized in Table 1. All the compounds investigated showed four quasi-reversible one-electron waves (except **11a** which exhibited an adsorption wave for the fully oxidized tetracationic species), the TTF moieties being oxidized sequentially at different potentials (see the supporting information).

The cation radicals **7b**$^{\bullet+}$, **10b**$^{\bullet+}$, **11b**$^{\bullet+}$, and **12b**$^{\bullet+}$ and the dication **12a**$^{2+}$, needed for optical and ESR spectroscopies, were subsequently easily generated in CH_2Cl_2 solution by controlled electrolysis at constant potentials.

(b) Optical Spectroscopy. Spectroscopic data (UV−vis and near-IR) are summarized in Table 2. For compounds **10b**$^{\bullet+}$ and **12b**$^{\bullet+}$, a broad and relatively intense band centered around 1600−1700 nm (Figure 2) is observed, whereas for compound **7b**$^{\bullet+}$, this band presents more structured features the maximum is displaced to higher wavelength, i.e. 2500 nm (Figure 3). It is worth noting that the nature of the substituent R has no dramatic influence on the electronic spectra. For the compounds **11**$^{\bullet+}$ no detectable intervalence band was measured. Interestingly, these near-infrared bands are not observed for either the neutral and or the dicationic forms of these bis(TTF) compounds.

In addition, for all three MV compounds investigated, an intense band centered around 950 nm appears for the dicationic species. This band, which vanishes upon dilution of the solution, is assigned to an intermolecular association phenomenon.[26] *On the contrary, the intensity of the intervalence bands in the spectra of the compounds* **7**$^{\bullet+}$, **10**$^{\bullet+}$, *and* **12**$^{\bullet+}$ *follows Beer's law over the concentration range* 2×10^{-5} *to* 2×10^{-4} *M,* indicating that these absorptions are not due to any aggregated forms of these cation radicals.[27]

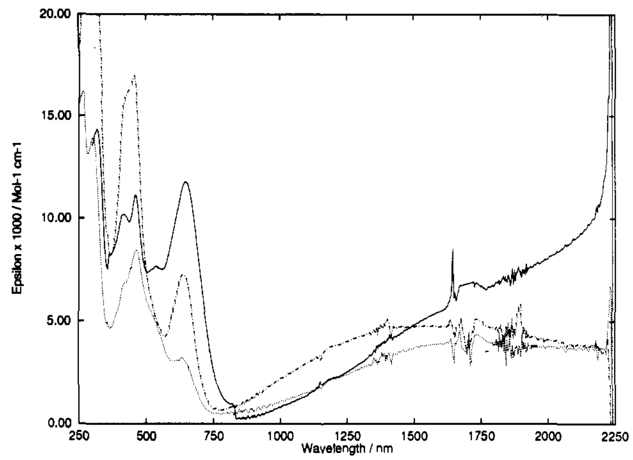

Figure 2. UV−vis/near-IR absorption spectra in dichloromethane (0.1 M nBu_4NPF_6) of **7b**$^{\bullet+}$ (1.7×10^{-4} M) (—), **10b**$^{\bullet+}$ (1.55×10^{-4} M) (-•-), and **12b**$^{\bullet+}$ (1.64×10^{-4} M) (•••) species obtained by one-electron constant-potential oxidations.

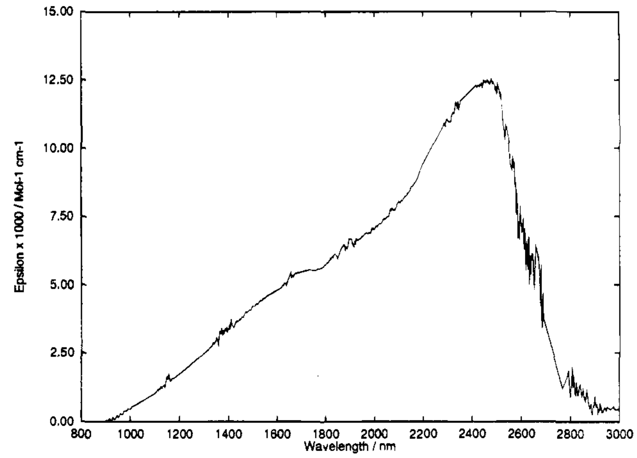

Figure 3. Near-IR absorption spectrum of **7b**$^{\bullet+}$ (1.7×10^{-4} M) in dichloromethane (0.1 M nBu_4NPF_6) after one-electron constant-potential oxidation.

(c) ESR spectroscopy.[28] The dichloromethane solutions of **10b**$^{\bullet+}$ exhibited, at room temperature, a single ESR signal (g = 2.008, ≅ 2 G peak to peak line width); a very similar spectrum was also obtained for the corresponding dication **10b**$^{2+}$.

(d) Calculations. The geometries of TTF and the bis(TTF) compounds have been optimized, both at the semiempirical AM1 and at the ab-initio SCF (MINI-1′) levels, and the results were qualitatively in good agreement. Closely similar bond length values were found for the parent TTF, and for the fused equivalent TTF subunits of compounds **7c**, **10c**, and **11c** (Figure 4; only **10c** is shown): C_5-C_6 double bond lengths were found equal to 1.351 Å for both TTF and the bis(TTF) compounds at

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(25) This unexpected result led us to reinvestigate our previous study on the regiochemistry of the substitutions of hexafluorobenzene by a related bidentate sulfur nucleophile (see: Gimbert, Y., Moradpour, A., Merienne, C. *J. Org. Chem.* **1990**, *55*, 5347); in this study only the corresponding linearly substituted regioisomer was isolated (41% yield). In fact, a more careful subsequent analysis of the reaction mixture led to the isolation by flash chromatography (eluting with CS_2 of the residue from the toluene mother liquors after recristallization of the linear regioisomer!) of a small amount (7% yield) of the 3-fold symmetry fully substituted ring (which we have synthesized later by another procedure; see: Gimbert, Y., Moradpour, A. *Tetrahedron Lett.* **1991**, *32*, 4897). The isolation of this fully substituted compound involves the formation of some (probably also around 10% yield) of the corresponding angularly substituted isomer that we missed in the first study.

(26) Torrance, J. B.; Scott, B. A.; Weber, B.; Kaufman, F. B.; Seiden, P. E. *Phys. Rev. B* **1979**, *19*, 730.

(27) (a) Ouahab, L; Fettouhi, M.; Halet, J. F.; Yartsev, V. M.; Garrigou-Lagrange, C.; Delhaes, P.; Sourisseau, C. *New J. Chem.* **1993**, *17*, 399. (b) Cooke, G.; Dhindsa, A. S.; Song, Y. P.; Williams, G.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A.; K.; Petty, M. C.; Yarwood, J. *Synth. Met.* **1993**, *55*−*57*, 3871.

(28) The present very short account of the ESR behavior of this series will be subsequently developed in a specific detailed study.

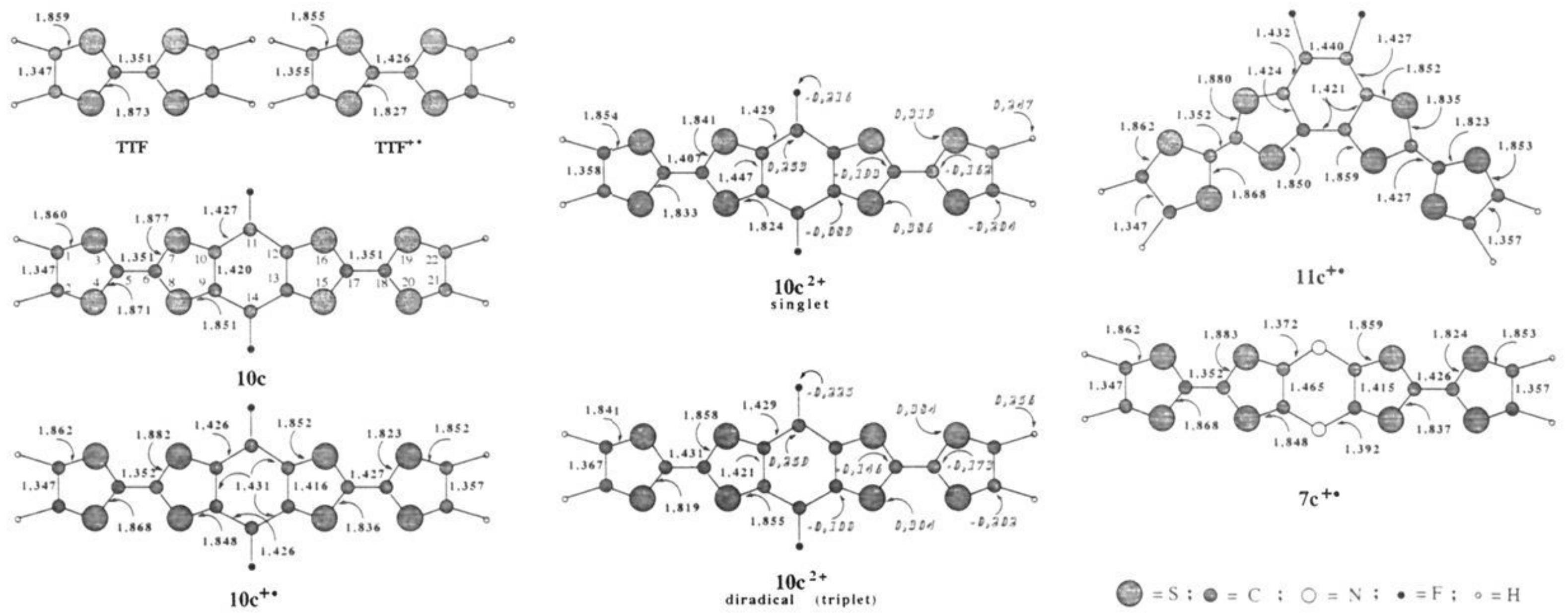

Figure 4. Calculated geometries, at the ab-initio (MINI-1′) level, of TTF, TTF$^{•+}$, **10c**, the cation radicals from the series of considered bis(TTF) compounds, and the **10c**$^{2+}$ singlet, and diradical (triplet). For both symmetrical **10c**$^{2+}$ structures the geometries and the charge partitions (to the right, shadow type) are included.

Table 3. Calculated[a] Total Energies, Charge Partitions (CP), and Spin Densities of the Cation Radicals **10c**$^{•+}$, **11c**$^{•+}$ ($^2B_1$), and **7c**$^{•+}$($^2A''$) Ground States

compd	*E*(total)[b]	CP1[c]	CP2[c]	spin density[d] description
7c$^{•+}$	−3725.549 633	0.398	1.006	$C_{17} > S_{19} = S_{20} > C_{18} > S_{15} = S_{16}$
10c$^{•+}$	−3890.266 276	0.382	1.024	$C_{17} > S_{19} \geq S_{20} > C_{18} > S_{15} \geq S_{16}$
11c$^{•+}$	−3890.261 669	0.358	1.007	$C_{17} > S_{19} = S_{20} > C_{18} > S_{15} = S_{16}$

[a] UHF-SCF (MINI-1′) level. [b] In hartrees. [c] CP1 is the sum of the net charges carried by C_1 to S_8 atoms and CP2 by S_{15} to S_{22} atoms, the hydrogen net charges being included (see **10c** in Figure 4 for the atom numbering). [d] The decreasing order of the unpaired electron spin density is given.

Table 4. Calculated Energies[a] of the Highest Occupied Spin Orbitals[b] (H_α, H_β) as Well as the Unpaired α One (Upα)

compd	H_α	H_β	Up_α
TTF$^{•+}$	−12.94 (52)	−14.10 (51)	−12.94 (52)
7c$^{•+}$	−10.36 (109)	−10.36 (108)	−13.17 (106)
10c$^{•+}$	−10.24 (117)	−10.24 (116)	−13.15 (114)
11c$^{•+}$	−10.38 (117)	−10.40 (116)	−13.26 (114)

[a] In eV. [b] Corresponding orbital numbering in parentheses.

the ab-initio MINI-1′ level (1.337 Å for TTF and 1.343 Å for the bis(TTF) compounds at the AM1 level).

A dramatic difference was found for TTF$^{•+}$, as compared to the cation radicals **7c**$^{•+}$, **10c**$^{•+}$, and **11c**$^{•+}$: while TTF, TTF$^{•+}$, and bis(TTF) compounds **7c** and **10c** belong to the D_{2h} point group (C_{2v} for **11c**), a symmetry breakdown occurred for the corresponding cation radicals, leading to C_{2v} **7c**$^{•+}$ and **10c**$^{•+}$ structures (C_s for **11c**$^{•+}$). This point group modification came from a significant elongation of *only one* of the central bond of one of the fused TTF compounds (Figure 4; compare C_5-C_6 to $C_{17}-C_{18}$ for **7c**$^{•+}$, **10c**$^{•+}$, and **11c**$^{•+}$). The value of these elongated bonds (1.427 Å for $C_{17}-C_{18}$) is now similar to the corresponding value for TTF$^{•+}$ (1.426 Å), while the corresponding bond of the second fused TTF (C_5-C_6) remains close to the value of the neutral TTF (1.351 Å). These remarkable bond-length modifications were also reflected in the net *charge partitions* (CP), calculated at the UHF-SCF (MINI 1′) level for these *localized* cation radicals (Table 3). The symmetries of the latter ground-state wave function are, respectively, $^2B_1$ (**7c**$^{•+}$, **10c**$^{•+}$) and $^2A''$ (**11c**$^{•+}$).

The spin densities were found to be spread specifically over the S_{15} to S_{20} fragment, the highest value being located on C_{17} (see **10c** in Figure 4 for the atoms numbering). The analysis of the ab-initio MINI-1′ results, considering the various calculated HOMO vs SOMO energies, led to an unexpected result (Table 4), also obtained at the UAM 1 level: the highest α and β spin orbitals (H_α and H_β) for the bis(TTF) compounds, **7c**$^{•+}$, **10c**$^{•+}$, and **11c**$^{•+}$ are paired at similar energies (∼−10 ev), while the unpaired spin orbital Upα corresponds to a lower energy (∼−13 ev); for TTF$^{•+}$, the Upα orbital (H_α) is, as expected, the highest one (−12.94 eV). It is worth noting that all the Upα energies lie in the same range for TTF$^{•+}$ and bis(TTF)$^{•+}$ compounds.

Considering further the dicationic oxidation stage of the bis(TTF) compounds, a similar geometry optimization of **10c**$^{2+}$ was also computed. Two stable electronic states corresponding, respectively, to a singlet and to a triplet (diradical) were obtained. These belong to the highly symmetrical D_{2h} point group, as already found for the parent bis(TTF) **10c**. The fulvalenic bonds for **10c**$^{2+}$ are now *equally* elongated, as compared to **10c**$^{•+}$(Figure 4). These bond lengths (compare C_5-C_6 for the **10c**$^{2+}$ singlet and triplet) are however significantly different for these two electronic configurations (1.407 Å for the singlet and 1.431 Å for the triplet). Simultaneously, the corresponding charge distributions of both **10c**$^{2+}$ structures are now symmetrically partitioned, mainly over the TTF moieties, and for the triplet **10c**$^{2+}$ the unpaired electron spins are also symmetrically distributed on the S_3, S_4, C_5, and C_6 (S_{19}, S_{20}, C_{17}, and C_{18}) atoms. Very interestingly the triplet (diradical) ground state was found to be more stable than the **10c**$^{2+}$ singlet structure, lying 54.15 kcal below the latter.[29]

Possible excited states of the considered cation-radicals were subsequently investigated, starting at the CIS level, which gives a first qualitative insight into their nature and energetics. Such CIS calculations, starting with the $^2B_1$ and $^2A''$ ground states, at optimized geometries of the bis(TTF) cation radicals provided two low-lying $^2B_1$ ($^2A''$) excited states; the same approach was also used for TTF$^{•+}$ and led to a $^2B_{2g}$ excited state, $^2B_{3u}$ being the ground state (Table 5). The corresponding transition, associated now with a symmetry change, was calculated at 461 nm.[30]

Using the information from these CIS-developed excited states, adequate permutations of occupied and virtual ground-state molecular spin orbital, allowed a better determination of

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(29) The existence of this new ground-state triplet has to be further corroborated experimentally; for other precedents of high-spin organic molecules, see for example: Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 1979.

Table 5. Calculated energies at the CIS level (*E*(excit)), Associated Wavelengths (λ) of the Ground $^2B_1$ ($^2A''$) to Excited $^2B_1$ ($^2A''$) State Transitions of **7c**$^{\bullet+}$, **10c**$^{\bullet+}$, and **11c**$^{\bullet+}$, the $^2B_{3u}$ to $^2B_{2g}$ calculated[a] transition of TTF$^{\bullet+}$, and the related oscillator strengths (*f*)

compd	*E*(excit)[a]	λ[b]	f[c]
TTF$^{\bullet+}$	2.691	461	0.201
7c$^{\bullet+}$	2.216	560	0.266
	2.940	422	0.092
10$^{\cdot+}$	2.237	554	0.210
	2.881	430	0.129
11$^{\cdot+}$	2.249	551	0.023
	2.676	463	0.281

[a] In eV. [b] In nm. [c] In a.u.

Table 6. $^2B_1$ ($^2A''$) Ground- to Excited-States Transition Energies (*E*(excit)) and the Associated Wavelength (λ), Net Charge Partitions (CP), and Spin Densities Calculated at the UHF-SCF (MINI-1′) Level

compd	*E*(excit)[a]	λ[b]	CP1[b]	CP2[c]	spin density[d] description
7c$^{\bullet+}$	0.556	2231	1.004	0.396	C6 > S3 = S4 > S7 = S8 > C5
10c$^{\bullet+}$	0.510	2432	1.020	0.384	C6 > S3 = S4 > S7 = S8
	0.555	2233	0.763	0.618	C5 > S7 = S8 > S19 = S20 > S3 = S4
11c$^{\bullet+}$	0.206	6025	1.034	0.323	C6 > S3 > S4 > S8
	0.366	3491	1.018	0.344	C6 > S3 > S4 > S8 ≥ S7 > C5
	0.366	2572	1.018	0.344	C6 > S3 > S4 > S8 ≥ S7 > C5
	0.366	2410	1.018	0.344	C6 > S3 > S4 > S7 ≥ S8

[a] In eV. [b] In nm. [c] See note c, Table 3. [d] See note *d*, Table 3.

excited states at the UHF-SCF level. These calculations led to several neighboring low-lying states, and thus provided two states for **10c**$^{\bullet+}$, four for **11c**$^{\bullet+}$, and only one for **7c**$^{\bullet+}$. The calculated ground- to excited-state energies, the corresponding wavelengths, and the related net charge partitions and spin density distributions are summarized in the Table 6.

Moreover, the UHF-SCF (MINI-1′) electronic ground-state wavefunction presented an intrinsic instability.[22] The further wave function optimization led to new net charge partitions, though with values very similar to the previously found nonoptimized ones. However, greater modifications in the accompanying spin distributions were found, emphasizing the new non-symmetric character of the optimized wave function. Furthermore, the average value of the total angular spin moment squared operator S^{**2} was greatly modified within this wave function optimization, from 0.75 to 1.71 (**7c**$^{\bullet+}$), 1.54 (**10c**$^{\bullet+}$), and 1.99 (**11c**$^{\bullet+}$).

Discussion

The presently synthesized series of bis(TTF) compounds exhibit interesting redox behavior that is typical of two electronically *interacting* electrophores. This behavior, as already observed in similar systems containing TTF subunits coupled via a π-conjugated ring,[14] is illustrated by the existence of quasi-reversible four-wave voltammograms (Table 1) and accounts for stepwise formation of all the identified robust one-electron oxidation intermediates, from the neutral bis(TTF) to the fully-oxidized tetracationic species. On the contrary, for the known compounds containing the TTF units linked by nonconjugated bridges,[31] the two TTF electrophores behave independently: no Coulombic repulsion is detected between the two positively-charged moieties formed in the oxidation steps, and both TTF electrophores are consequently oxidized at the same potential, resulting in two two-electron waves.

When the literature results of the compounds, exhibiting mixed-valence properties, are now considered,[2,3,7,11] an electrochemical behavior, involving both one-electron and/or multielectron wave voltammograms is found. Thus, for the series of Ru–L–Ru dimers[12,32] which undergo two one-electron oxidations, separate values for the corresponding half-wave potentials are only observed in a limited number of cases, depending on the nature of the link L, and two-electron wave voltammograms are common. For the organic mixed valence compounds the same situation prevails: i.e., one- and two-electron wave voltammograms for **5**[9] and two-electron wave voltammograms for **4**[8b] and **6**[11b] (Chart 2) have been observed. However, such nonresolved multielectron transfers and/or the possibility to equilibrate the MV state with the corresponding isovalent states (as observed, for example, in the studies on the above-mentioned ruthenium dimers[12,32]) involved generally rather heavy procedures[33] needed to generate, identify, and study the MV species. Consequently, the existence of strongly interacting electrophores, involving exclusively one-electron processes, is not mandatory for mixed valency. But, the present series of bis(TTF) compounds, exhibiting such sequential formation of all the oxidized intermediates, allows, by an electrochemical means, the cation radical (trication radical) MV stages to easily be reached.[15] The observation of the broad (width at half-height 5000 cm^{-1}) and moderately intense ($\epsilon \cong$ 5000 M$^{-1}\cdot$ cm^{-1}) near-IR absorption bands, not detected from the bis(TTF) dications, is now straightforward from the cation radicals. Moreover, the shape and the intensity of these bands is an indication[34] of a class II (i.e., localized) electronic structure of the latter MV compounds.

The results of our calculations clarified these unexpected properties, at least at the origin of this work,[35] of our cation radicals. The first aspect concerned the ground-state geometries of the bis(TTF)$^{\bullet+}$ compounds as compared to TTF$^{\bullet+}$, and the bis(TTF)$^{2+}$ compounds. The conformation of TTF$^{\bullet+}$ and also

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[30] This calculated value is clearly overestimated, the actual optical transition of TTF$^{\bullet+}$ occuring at 580 nm (ref 26). This fact emphasizes the qualitative aspect of the results yielded by the CIS method using a singly-excited electronic configuration development based on poorly adapted MOs for the excited-states description.

[31] See for example: Wang, C.; Ellern, A.; Becker, J. Y.; Bernstein, J. *Tetrahedron Lett.* **1994**, *35*, 8489 and references cited therein.

[32] Ribou, A. C.; Launay, J. P.; Takahashi, K.; Nihira, T.; Tarutani, S.; Spangler, C. W. *Inorg. Chem.* **1994**, *33*, 1325 and references cited therein.

[33] Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107 and references cited therein.

[34] The simple Hush model,[4] correlating the IT band energy with bandwidth, gave us a first qualitative insight into the MV behavior, by means of the electronic coupling parameter V_{ab}. The latter was obtained from the following equation for the oscillator strength *f*, needed here because of the non-Gaussian shape of the measured bands (see, i.e., Figure 3):

$$f = 4.321 \times 10^{-9} \int \epsilon \, d\bar{\nu} \quad \text{and} \quad f = 1.085 \times 10^{-5}\, \bar{\nu} D^2 \qquad (1)$$

The integration has to be carried out over the whole absorption band, ϵ (M^{-1} cm^{-1}) is the usual molar extinction coefficient, ν or E_{op} corresponds to the band absorption maximum (cm^{-1}), and *D* (Å) corresponds to the dipole strength:

$$D = V_{ab} e R / E_{op}$$

The factor *R* is defined as the distance between the two redox sites, presumed to be punctual, in this oversimplified treatment. One obtains therefrom

$$V_{ab}\ 1.9951 \times 10^{-2} \left[\left(E_{op} \int \epsilon \, d\bar{\nu}\right)/R^2\right]^{1/2}$$

A tentative value for *R*, assumed to be roughly equal to 8.6 Å for both **7b**$^{\bullet+}$, **10b**$^{\bullet+}$, and **12a**$^{\bullet+}$, and the estimation of the absorption-band areas led to V_{ab} = 785 cm^{-1} (ν = 4000 cm^{-1}) for **7b**$^{\bullet+}$, V_{ab} = 1000 cm^{-1} (ν = 6000 cm^{-1}) for **10b**$^{\bullet+}$, and V_{ab} = 800 cm^{-1} (ν = 5750 cm^{-1}) for **12a**$^{\bullet+}$. These V_{ab} values, corresponding approximately to 15–20% of the optical-transition energies, are an indication of a class II behavior, while a class III compound would give a V_{ab} value of at least 50%.

10c^{2+}, an ESR active diradical, remain completely symmetrical, while the bis(TTF)$^{•+}$ compounds are computed as *distorted* structures (Figure 4) with an excess charge trapped on one of the TTF moities (CP1 vs CP2, Table 3). Other examples of such an a priori surprising localization phenomenon within fully conjugated π-systems are seldom: (i) the localization of the unpaired electron within the anion radicals **5** ($n = 3$) was first speculatively hypothetized[9b] and later elegantly demonstrated by low-temperature EPR studies[9d] which provided definite evidence for this phenomenon; (ii) comparing the oxidation redox potentials of several extended bis(TTF) donors to the parent "mono" (TTF) compounds,[14] the lack of significant differences between these values, that is, the absence of any extra charge stabilization due to the extended conjugation, was attributed to a "localization of the excess charge in one of the two TTF subunits",[14] but no other conclusions were drawn from this interesting observation.

Our present results clearly indicate that, while TTF$^{•+}$ and bis(TTF)$^{2+}$ (i.e., **10c**$^{2+}$) charge and spin distributions are *fully delocalized*, the bis(TTF)$^{•+}$ ones are localized, and the latter compounds can be considered as *mixed-valence species*. This condition, prerequisite to the assignment of the broad low-energy transitions displayed by these valence-trapped species, and lacking for the delocalized ones, to an intervalence band, is now fulfilled.[3,4]

Further investigations of the MO picture of the ground and excited states of these bis(TTF)$^{•+}$ compounds gave a more detailed description of such optical transitions. Here, several factors indicated the existence of *nonadiabatic*[36] (NA) and spin-orbit[37] (SO) *couplings* between these, close to one another, electronic states (vide infra). The first factor was clearly the very high difficulty to find one single well-defined excited doublet state at the UHF-SCF level (Table 6). Secondly, the ground-state instability analysis, effected by a CIS-like development, showed perturbations by one or two $^4A_2$ states, as emphasized by the corresponding eigenvectors. These happened to present the same CI developments as the second and fourth excited states (only the second is included in Table 5) obtained by CIS calculations.[38] Furthermore, the new nonsymmetric character of the optimized ground-state wave function, obtained in this instability analysis, may also be linked with a possible NA coupling. These couplings must, in fact, effectively involve the ground state; and, depending on whether the UHF-SCF MO description converges, two kinds of interesting results were obtained, by chance (Tables 3 and 6): (i) excited states located at ca. 0.4 eV above the ground state were found, the corresponding charge partition being inversed (compare CP1 and CP2) and the spin densities swept from one side to the other; (ii) states with unchanged charge partitions, actually the ground state itself, were computed. The first case highlights the charge-transfer processes between the two electrophores, and offers a nice theoretical description of an intervalence transition, obtained for the first time at the ab-initio level.

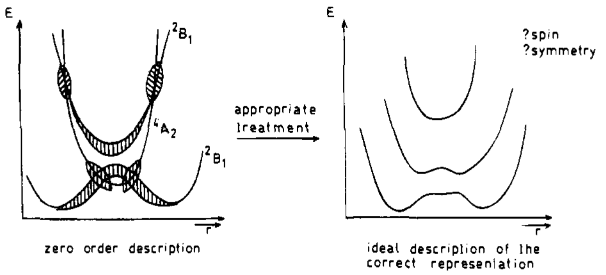

Figure 5. General electronic coupling scheme. The zero-order description refers to the SCF level, and the coordinate $\vec{r}$ might be thought of as mainly involving the bond elongations along C_5-C_6 and shortenings along $C_{17}-C_{18}$. The double minimum graph used to symbolize the ground-state doublet is related to the unsymmetrical localization of the bis(TTF)$^{•+}$ charge distribution at their optimized geometries. The calculation of the exact values of the energy barrier between the two wells is not possible at this zero-order description.

The NA and SO couplings between the ground and first excited electronic states of the bis(TTF)$^{•+}$ compounds are summarized in a schematic representation (Figure 5). Such interactions are consequences of the existence of (i) (for NA couplings) several electronic states lying in a small energy range and implying a high level of dependence—usually not considered within the Born–Oppenheimer (BO) approximation—of the electron wave function characteristics on the nuclear coordinate variations; (ii) (for SO couplings) relativistic effects related to orbital and intrinsic spin-interacting magnetic moments. These couplings result in a mixing of both the electronic repartition and the electronic spin states and lead to new states that cannot be properly described at the SCF level (zero-order description). To remain in the BO framework, the calculations of the electronic states, and the corresponding transition probabilities between them, would require the use of more sophisticated and heavy methods, such as post-SCF CISD or MCSF-CI methods, whose use with the present extended molecular systems is unthinkable.

Several aspects of the calculated intervalence transitions (Table 6) displayed by the bis(TTF)$^{•+}$ compounds may now be emphasized: (i) The number of very close excited states found at the UHF-SCF level (Table 6) for each cation radical probably reflects the *strength* of the corresponding NA and SO couplings, illustrated by the enlarged regions on the diagram (Figure 5). These coupling strengths are therefore very unequivalent for **7c**$^{•+}$, **10c**$^{•+}$, and **11c**$^{•+}$. For **11c**$^{•+}$ the broadest calculated transition (λ from 6025 to 2410 nm) would correspond to the existence of the greatest NA coupling. (ii) The oscillator strength values, as calculated only at the CIS level, also highly depended on the structures of the compounds (Table 5); the value found for **11c**$^{•+}$ ($f = 0.023$) is very low; and the corresponding very broad transition (undetectable experimentally) is therefore predicted to be of low intensity. Such behavior of the latter cation radical, though also exhibiting localized calculated charge partitions (see CP1 and CP2, Tables 3 and 6), illustrates a smaller optical IT "communicability" of these valence-trapped moieties, as already observed for other intervalence transitions involving "meta" substitution effects.[39] (iii) The other calculated transitions, as illustrated by the associated wavelengths (Table 6) for **7c**$^{•+}$ and **10c**$^{•+}$, are in good qualitative agreement with the actually observed transitions (Table 2, Figures 2 and 3).

In summary, our results allow the low-energy near-IR bands exhibited by the mixed valence (class II) compounds **7b**$^{•+}$,

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(35) The present series of compounds were designed and synthesized as potential extended-TTF donors toward the preparation of new conducting organic solids; these are usually built on from unsaturated fully delocalized components. The influence of the localization, at the molecular level of the building blocks, on the conductivity of the solids therefrom has never been, to our knowledge, examined.

(36) For calculation of nonadiabatic processes, as applied to a small triatomic molecule, see: Dehareng, D.; Chapuisat, X.; Lorquet, J. C.; Galloy, C.; Raseev, G.; *J. Chem. Phys.* **1983**, *78*, 1246. See also: Desouter-Lecomte, M.; Dehareng, D.; Leyh-Nihant, B.; Praet, M. Th.; Lorquet, A. J.; Lorquet, J. C. *J. Phys. Chem.* **1985**, *89*, 214.

(37) (a) Bransden, B. H. ; Joachain, C. J. *Physics of Atoms and Molecules*; Longman Science & Technology; Wiley: New York, 1983. (b) Remacle, F.; Petitjean, S.; Dehareng, D.; Lorquet, J. C. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 187.

(38) The real number of electronic states involved in the different couplings was not determined.

(39) Richardson, D. E.; Taube, H.; *J. Amer. Chem. Soc.* **1983**, *105*, 40.

10b$^{\bullet+}$, and **12b**$^{\bullet+}$ to be unambiguously assigned, to intervalence transitions. The occurrence of such transitions also implies also the close proximity of the excited states which happen to be nonadiabatically coupled to the ground-state of these species. The mixed valence extended-TTF compounds, whose properties are tunable by changing the nature of the bridge between the TTF electrophores, are therefore new interesting near-IR dyes.[40] Beyond this aspect,[41] unexpected localization effects might also exist within other highly conjugated organic substrates, and could consequently be considered in the studies of various abiotic and also probably biological processes involving such electron transfer mediators.

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Supporting Information Available: Figures showing the cyclic voltammetry results for compounds **7**, **10b**, **11a**, and **12a** (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(40) (a) Fabian, J.; Zahradnik, R. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 677. (b) Fabian, J.; Nakazumi H.; Matsuoka, M. *Chem. Rev.* **1992**, *92*, 1197.

(41) As suggested by a reviewer, our mixed valence bis(TTF) compounds, and analogously the quinones studied by Miller, might also be viewed as donor/acceptor substituted species (i.e., electron-rich neutral TTF fragment vs electron-poor local cation radical, and similarly for **5**, electron-rich anion radical fragment vs electron-poor neutral quinone). Of course, this picture implies unusual *localized* electronic structures, and the scope of this model awaits further studies. In fact, actual donor/acceptor substituted substrates have been used as near-IR dyes (see ref 40b and the references cited therein).