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Synthesis of Several Isomeric Tetrathiafulvalene π-Electron Donors with Peripheral Sulfur Atoms. A Study of Their Radical Cations

Concepció Rovira,* Jaume Veciana, Nuria Santaló, Judit Tarrés, Joan Cirujeda, Elies Molins,
Jordi Llorca, and Enrique Espinosa

Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., 08193 Bellaterra, Spain

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An efficient synthesis of one new (10) and three previously reported (9, 11, and 12) π-electron donors, which have one sulfur atom in each of the outer five-membered rings attached to the TTF system, is presented. The radical cations derived from 9–11 have been studied by ESR spectroscopy and the spin density distribution of these radical cations, as well as those of other related radical cations, have been determined by MO calculations and correlated with the ESR spectral data. The single-crystal X-ray structures of π-donors 9 and 12 are reported. The most remarkable fact of these structures is the transverse intermolecular contacts between interstacked molecules. The external sulfur atoms of 9 play a central role in its transverse structural pattern. Complexes of donors 9 and 10 with tetracyano-*p*-quinodimethane (TCNQ) and tetrafluorotetracyano-*p*-quinodimethane (TCNQF$_4$) have been obtained and characterized.

Since the discovery of the first sulfur-based organic superconductor (BEDT-TTF)$_2$ReO$_4$,[1] the synthesis of new multicalcogen π-electron donors has remained at the forefront of research in the field of organic metals.[2] Some of these molecules provide radical cation salts which are superconductors,[3] being bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) the donor that forms the salt with the highest T_c, 12.8 K.[4] Intermolecular interactions between multisulfur π-donor molecules usually enhance the dimensionality of their salts permitting the suppression of metal–insulator (M–I) transitions and, therefore, allowing that transitions to the superconducting state occur.[5] The outer sulfur atoms in these molecules play an essential role in such intermolecular interactions and their position as well as the size of the cyclic substituents of the TTF skeleton are features that influence outstandingly the electronic properties of the heterofulvalenic π-system.[6] Consequently, the synthesis of new multisulfur π-donors as well as the preparation of their charge transfer salts and complexes are of great interest. We now describe the synthesis of four distinct π-donors: bis(ethylenethio)-tetrathiafulvalene (BET-TTF) **9**, bis(thiodimethylene)-tetrathiafulvalene (BTDM-TTF) **10**, dithiophenetetrathiafulvalene (DT-TTF) **11**, and α-dithiophenetetrathiafulvalene (α-DT-TTF) **12**; all of them with one outer sulfur atom in each of the cyclic substituents of the TTF core.[7] Compounds **9** and **10** and their aromatic counterparts, compounds **11** and **12**, are isomers that only differ in the position of their external sulfur atoms; this small difference, could provoke, however, differences in their electronic properties and introduce a great disparity in the crystal packings and therefore in the electric properties of their charge transfer salts and complexes. For such reason besides the preparation of compounds **9–12**,[8] we have studied their solution electrochemistry by the cyclic voltammetry technique, characterized and studied their radical cation derivatives by ESR spectroscopy and MO calculations, and determined the X-ray crystal structures of donors **9** and **12**. The formation of TCNQ and TCNQF$_4$ charge-transfer complexes with the nonaromatic donors **9** and **10** have also been undertaken.

The syntheses of π-donors are presented in Scheme 1. As described previously for other TTF derivatives the key step in this synthetic route is the formation of thiones by the thermolysis of the corresponding 1,2,3-thiadiazoles and the subsequent trapping of the formed 1,3-dipoles by carbon disulfide.[9] The starting material in this route is the tosylhydrazone of tetrahydrothiophen-3-one (**1**) that was obtained in a E/Z proportion of 1:1, as ascertained by

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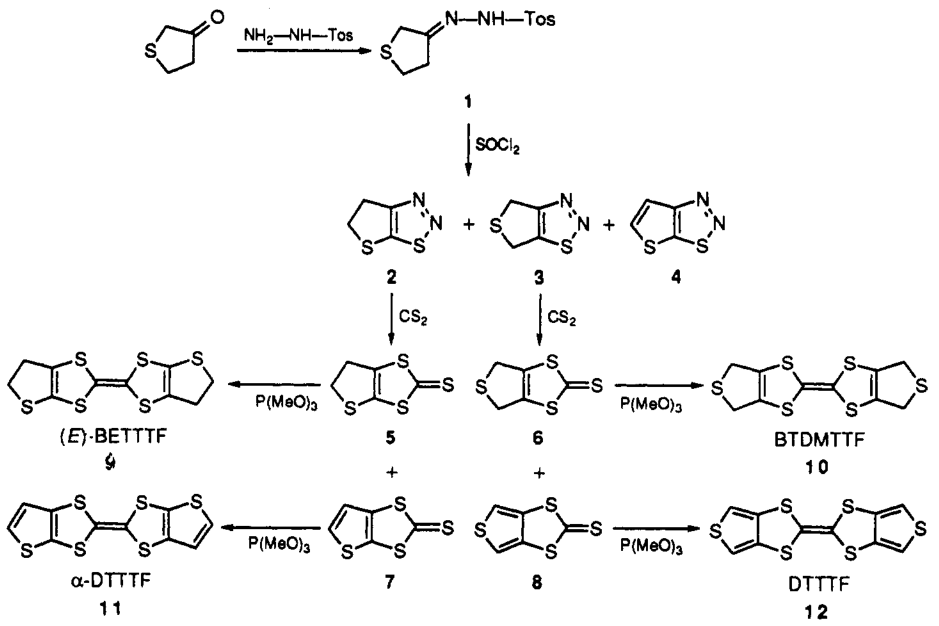
Scheme 1



^{1}H NMR. Treatment of **1** with tosyl chloride[10] gives a mixture of 1,2,3-thiadiazole isomers **2** and **3** in a **2**/**3** proportion of *ca.* 2:1. The sulfur atom of the tetrahydrothiophene cycle of **1** does not promote any high regioselectivity on the ring closure to form the corresponding thiadiazole derivatives, in contrast with the cyclization of 1-thia-3-cyclooctanone semicarbazone, promoted by SeO$_2$, that has a very high regioselectivity (the proportion of isomers usually found is 1:50).[11] Besides compounds **2** and **3**, the aromatic analog of **2**, thieno[3,2-*d*]-1,2,3-thiadiazole (**4**),[12] was also obtained in a growing proportion with the increase of the reaction time. Thiadiazoles **2**–**4** were separated by recurrent column chromatography. Thermal decomposition of thiadiazoles **2** and **3** in the presence of carbon disulfide provides the expected 1,3-dithiole-2-thiones **5** and **6**, respectively, and a small amount of the corresponding aromatic thiones **7** and **8**. The amount of aromatic thiones and the conversion of starting materials strongly depends on the reaction conditions (temperature, pressure, and time). The aromatic thiones **7** and **8** have also been obtained by sulfur dehydrogenation at 150 °C of the dihydrothieno derivatives **5** and **6** in carbon disulfide solutions.[13]

Each one of thiones **5**–**8** were coupled in neat boiling trimethyl phosphite to give the corresponding tetrathiafulvalene derivatives **9**–**12** in moderate to poor yields. This procedure is the simplest way to convert dithiolanethiones into tetrathiafulvalenes,[14] and only for compound **11** did it seem more convenient to use the Engler's two-step route using the same precursor.[7a] By coupling of thione **5** only the *E* isomer of **9** was obtained as a red microcrystalline powder that precipitates from the phosphite solution. The structure of this isomer was determined by X-ray diffraction in such a way confirming its *E* nature. Engler et al.[7a] have previously reported that trialkyl phosphite promotes the coupling of the dithiolane selone analogues of **5** producing both *E* and *Z* isomers of **9**. However, at this time both isomers were not completely and unambiguously characterized, probably due to their intrinsic low solubility and to the low sensitivity and resolution of the spectral techniques used by those authors. As it was previously observed for other substituted tetrathiafulvalenes,[15] compound (*E*)-**9** isomerizes very rapidly in acidic solutions giving rise to *E*/*Z* isomeric mixtures. This isomerization is readily observed by comparing the ^{1}H NMR spectrum of pure (*E*)-**9** in d_6-DMSO and commercial CDCl$_3$ containing HCl traces. Thus, in the first solvent only lines of the *E* isomer were observed while in the acidic media superposed lines of both isomers are present. This type of isomerization has been postulated to occur through an equilibrium with the corresponding protonated TTF derivative and recently, an example of this protonated species, the tetrathiafulvalenium ion, has been isolated and completely characterized as its tetrafluoroborate salt.[16] Our efforts to isolate the tetrafluoroborate salt of protonated **9** have been so far unsuccessful.

The molecular structures of compounds **9** and **12**, are shown in Figure 1 together with their atomic numbering schemes. Both molecules are quasiplanar showing only a low distortion toward a chair conformation (Figures 2b and 3b). Angles between the external rings and TTF core double bonds mean planes are 2.0° for compound **9** and 3.0° for compound **12**. The deviation from the planarity of **9** is by far the lowest observed for any other sulfur-substituted TTF derivatives such as BEDT-TTF[17] and DMET.[18]

The crystal packing of **9** shows that molecules are stacked along the *c* axis, without any significant intrastack overlap. Short intermolecular S···S contacts, lower than the sum of the van der Waals radii, are only found in the *ab* plane

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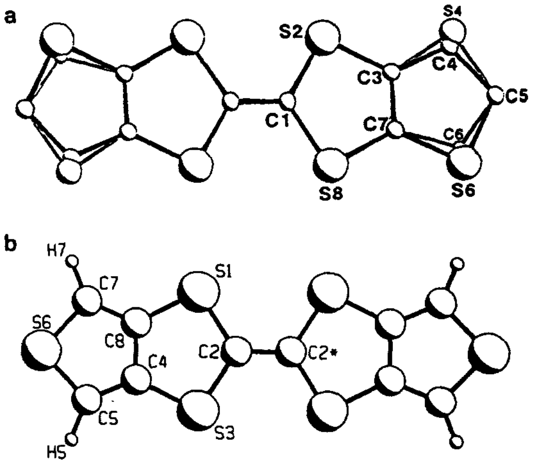

Figure 1. (a) Molecular structure of compound **9** showing the atomic labeling and the disorder observed in the crystal packing (15%) for S_6–C_6 and S_4–C_4 atoms. (b) Molecular structure of compound **10** showing the atomic labeling.

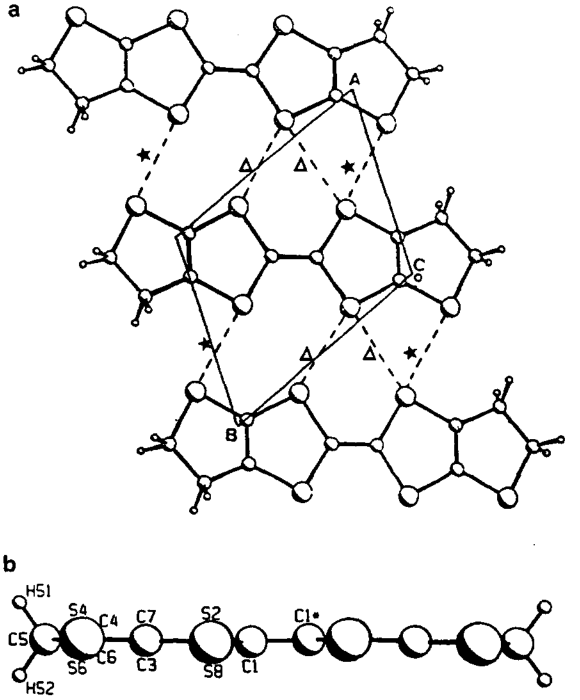

Figure 2. (a) X-ray crystal packing of compound **9** showing intermolecular short $S\cdots S$ contacts (★) $3.456 < S\cdots S < 3.458$ and (△) $3.560 < S\cdots S < 3.562$. (b) X-ray crystal structure of compound **9** viewed parallel to the plane of TTF moiety.

between molecules belonging to parallel stacks, these contacts being shorter than those showed by BEDT-TTF.[16] The external sulfur atoms of **9**, together with the sulfur atoms of the TTF core, play a central role for the formation of these characteristic transverse intermolecular contacts (Figure 2a).

Molecules of compound **12** stack uniformly along the *b* axis in a herringbone pattern (Figure 3a). Short intermolecular $S\cdots S$ contacts are also present in the crystal packing of **12**, occurring also between molecules of different stacks, although the external sulfur atoms in this molecule do not play a significant role in this association ($S_6\cdots S_6$ = 3.721 Å).

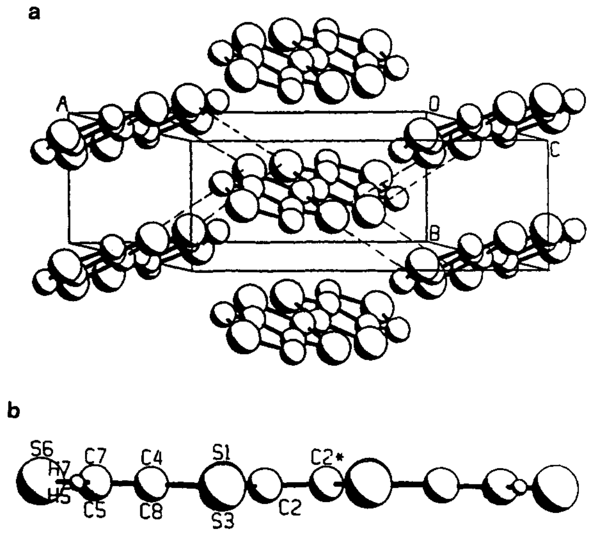

Figure 3. (a) X-ray crystal packing of compound **12** showing intermolecular short $S\cdots S$ contacts $S_1\cdots S_3$ = 3.547 Å. (b) X-ray crystal structure of compound **12** viewed parallel to the plane of TTF moiety.

Chart 1

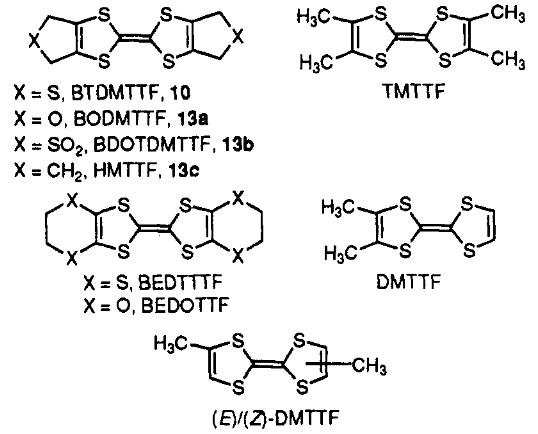

Table 1. Cyclic Voltammetric Data (in volts) of π-Donors 9–13[a]

compd	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
TTF	0.39	0.62	0.23
BODM-TTF, **13a**[b]	0.35	0.66	0.31
BDOTDM-TTF, **13b**	0.65	0.80	0.15
BET-TTF, **9**	0.43	0.58	0.15
BTDM-TTF, **10**	0.55	0.72	0.17
α-DT-TTF, **11**	0.50	0.67	0.17
DT-TTF, **12**	0.78	0.96	0.18

[a] Experimental conditions: rt; DMF/0.1 MTBAPF$_6$; vs SCE, Pt electrodes, 200 mV s^{-1}. [b] From ref 19.

The solution redox properties of donors **9–12** have been studied by cyclic voltammetry and the results are collected in Table 1 along with those obtained with related examples of the TTF family such as BODM-TTF (**13a**)[19] and BDOTDM-TTF (**13b**).[20] All compounds undergo two separate reversible one-electron oxidations. As occur with other thioalkyl-substituted TTF derivatives,[21] all the studied donors show a diminished electron donor ability with respect to TTF and, in addition, between pairs of isomeric donors **9–10** and **11–12**, those with the sulfur atoms in the α position with respect to the TTF core are

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Table 2. ESR Spectral Parameters[a]

compd (radical cation)	obsvd a_H	calcd[c] a_H	obsvd a_{33_S}	g
TTF[b]	0.125 (4H)	0.066 (4H)	0.425 (4S)	2.0081
BEDT-TTF[b]	≤0.005 (8H)	0.005 (8H)	0.370 (4S) ≤0.080 (4S)	2.0074
BDOTDM-TTF, **13b**[b]	0.158 (8H)	0.148 (8H)	0.425 (4S)	2.0077
HM-TTF[b,d]	0.211 (8H)	0.186 (8H)	0.420 (4S)	2.0078
TM-TTF[b,d]	0.074 (12H)	0.071 (12H)	0.395 (4S)	2.0078
DM-TTF[b,d,e]	0.118 (2H) 0.082 (6H)	0.056 (2H) 0.099 (6H)		
(*E*)/(*Z*)-DM-TTF[b,d]	0.132 (2H) 0.066 (6H)	0.101 (2H)[f] 0.028 (6H)[f]	0.435 (2S) 0.390 (2S)	2.0079
BET-TTF, **9**	0.257 (4H)	0.324 (4H)	0.425 (2S) 0.335 (2S)	2.0074
BTDM-TTF, **10**	0.130 (8H)	0.156 (8H)	0.425 (4S)	2.0079
α-DT-TTF, **11**	0.110 (2H) 0.021 (2H)[g]	0.085 (2H) 0.027 (2H)	0.406 (4S)	2.0071
DT-TTF, **12**[b]	0.020 (4H)	0.011 (4H)	0.405 (4S)	2.0077

[a] Hyperfine coupling constants, a_x, given in mT. [b] From ref 23. [c] Calculated using ZINDO/1 method. See text. [d] HM-TTF, hexamethylenetetrathiafulvalene; TM-TTF, tetramethyltetrathiafulvalene; DM-tetrathiafulvalene, 2,3-dimethyltetrathiafulvalene; (*E*)/(*Z*)-DM-TTF, 2,6- and 2,7-dimethyltetrathiafulvalene. [e] Surprisingly, MO calculations indicate that the higher H *hfcc* value corresponds to the ring protons, in contrast with the assignment previously given by F. Gerson et al.[23] [f] Mean value for the calculated *hfcc* of *Z* and *E* isomers, the values for such isomers being very similar. [g] Estimated value from ESR simulation.

easier to oxidize. As occurs for BEDO-TTF and BEDT-TTF donors in various solvents,[21b] between analogous donors BODM-TTF (**13a**) and BTDM-TTF (**10**) the compound with oxygen atoms in the external rings is easier to oxidize. A remarkable feature from the comparison of the data in Table 1 is that all donors with sulfur atoms in the outer five-membered rings substituent have small differences between the first and the second ionization potentials, owing to reduction of on-site coulombic repulsions. A clear indication that the on-site Coulomb repulsion *U* is small in BET-TTF (**9**), is the large conductivity value (10 S cm^{-1}, 300 K) that presents the fully transferred salt BET-TTF PF$_6$.[22]

Radical cations of donors **9**–**11** in solution have also been studied by electron spin resonance (Table 2). Oxidation of these donors was carried out by AlCl$_3$ in methylene chloride and the ESR spectra were recorded in the range 293–240 K. Decreasing temperature had only effect on the narrowing of line widths. All radical cations **9**$^{\bullet+}$–**11**$^{\bullet+}$ yielded intense satellite lines from which the isotropic hyperfine coupling constants, *hfcc*, of naturally abundant ^{33}S isotopes, a_{33}, were determined, values that were subsequently verified by computer simulation (see Figure 4).

The assignment of some of the coupling constants has been made by using the results obtained with MO calculations and also by analogy with the ^{33}S data of BEDT-TTF.[23] The geometries of the radical cations used for such MO calculations were optimized with the AM1 hamiltonian. The spin densities obtained from the optimized geometries were calculated with the UHF approximation, using the following four different methods: AM1, INDO, ZINDO/1, and MINDO/3. In order to test which one of these methods better reproduces the experimental values, calculations with some methyl- and methylene-substituted TTF, besides the radical cations **9**$^{\bullet+}$–**12**$^{\bullet+}$, were performed (Table 2). ZINDO/1 method gives the best agreements between the observed and calculated H *hfcc* as can be observed from the regression shown in Figure 5, although very good results were also obtained with the INDO method. By contrast, agreements using AM1 and MINDO/3 methods are very poor. Neither absolute values nor experimental trends observed for ^{33}S *hfcc* were well reproduced by any of the four tested methods. Thus, satisfactory absolute values are obtained with MINDO/3, but this method is unable to reproduce the tendency of *hfcc* and the opposite occurs with INDO and ZINDO/1.

A prominent feature in the ESR spectra of the studied radical cations is the substantial coupling constants observed for the four equivalent protons in the two CH$_2$ groups adjacent to the TTF moiety of **9**$^{\bullet+}$ that are twice of those observed for the four CH$_2$ groups of its positional isomer **10**$^{\bullet+}$. Also the H coupling constants observed for the two equivalent aromatic protons nonadjacent to the TTF moiety in **11**$^{\bullet+}$ are larger (0.110 ± 0.002 mT) than those of the adjacent protons in both **11**$^{\bullet+}$ (0.021 ± 0.006 mT) and **12**$^{\bullet+}$ (0.020 ± 0.001 mT). Concerning ^{33}S coupling constants, compound **10**$^{\bullet+}$ has the same *hfcc* value as all other π-donors with nonaromatic five membered rings attached to the TTF core reported in Table 2. Both aromatic-substituted TTF isomers **11**$^{\bullet+}$ and **12**$^{\bullet+}$ have the same *hfcc* values, compound **11**$^{\bullet+}$ having only one value of ^{33}S coupling constants. By contrast, compound **9**$^{\bullet+}$ presents clearly (see Figure 4a) two different values of ^{33}S *hfcc* corresponding to two equivalent pairs of sulfur atoms of the TTF core, one closer to the sulfur of the outer ring (0.335 ± 0.003 mT) and the other closer to the methylene group (0.425 ± 0.005 mT). The value of the last coupling constant is in addition the same as that presented by TTF compounds with methylene substituents whereas the smaller one is closer to that of BEDT-TTF radical cation. This interesting fact is in accordance with the existence of some spin density on the external sulfur atoms of **9**$^{\bullet+}$ and suggests that bidimensional band structures in their solid charge-transfer salts can be promoted.

Isomeric donors BTDM-TTF (**10**) and BET-TTF (**9**) form almost quantitatively crystalline charge-transfer complexes with TCNQ and TCNQF$_4$ with a 1:1 donor:acceptor stoichiometries confirming their π-electron donor abilities. Figure 6 shows absorption spectra of these charge-transfer complexes. Both TCNQ complexes show strong and broad bands around 3000 cm^{-1}, corresponding to the charge transfer bands characteristic of mixed valence states.[24] Complexes with the stronger acceptor TCNQF$_4$ do not show such a charge-transfer band, indicating completely ionized states for both components of the complexes. The degree of charge transfer, ρ, was estimated using the infrared stretching frequency of the nitrile group of TCNQ[25] and TCNQF$_4$,[26] being $\rho = 0.6$ for BTDM-TTF/TCNQ and BET-TTF/TCNQ, $\rho = 0.95$ for BTDM-TTF/TCNQF$_4$, and $\rho = 1.0$ for BET-TTF/TCNQF$_4$. In spite of considerable efforts, it was only possible to grow crystals of a quality and size large enough for single-crystal X-ray structure determination and conductivity measurements for the complex BTDM-TTF/TCNQ.[27] This compound

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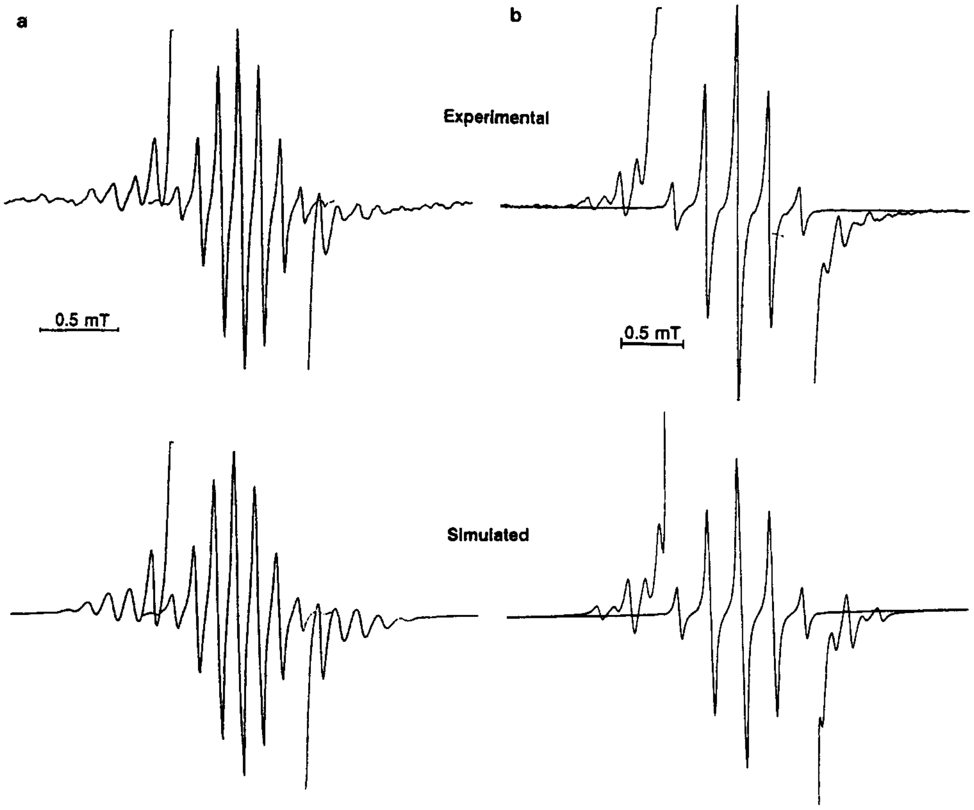

Figure 4. Experimental at 293 K and simulated ESR spectra of (a) compound $9^{\cdot+}$ and (b) compound $10^{\cdot+}$, showing the satellite lines due to the ^{33}S coupling constants. The computer simulations made use of the coupling constants given in the text and in the Table 2; line shape, Lorentzian; line widths, $9^{\cdot+}$, 0.060 mT; $10^{\cdot+}$, 0.055 mT.

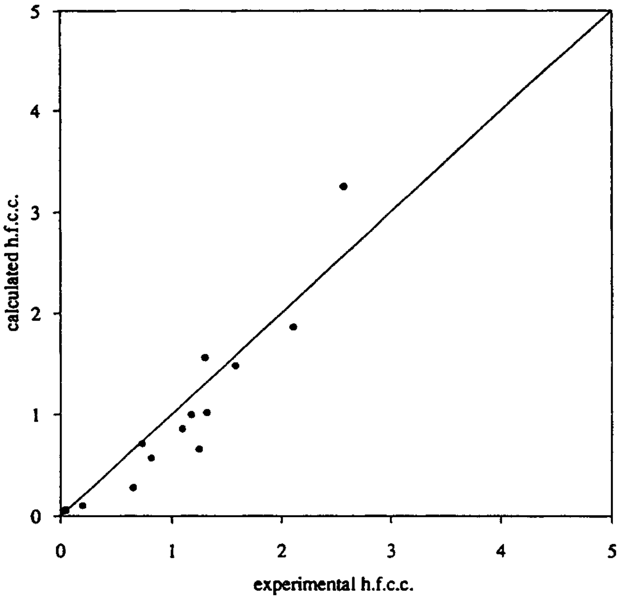

Figure 5. The correlation between observed and calculated *hfcc*, using the ZINDO/1 method, for protons of listed TTF derivatives. The least square linear regression of points gave a slope of 0.97 (r = 0.930).

has a metallic behavior down to 26 K with a room temperature conductivity of 130 S cm^{-1}, this value being comparable to those shown by most purely organic charge-transfer metals and the M–I transition temperature the lowest one observed for TCNQ complexes.

Experimental Section

Melting points were obtained with a Köfler microscope and are uncorrected. Microanalyses were performed at the Microanalysis Service of the Center d'Investigació i Desenvolupament, CSIC. MO calculations were performed using the HyperChem package without any modification.[28] UV-vis and IR spectra were measured on Perkin-Elmer Lambda Array 3840 and Perkin-Elmer 682 spectrometers, respectively. Vis-NIR spectra were measured on a Varian Cary 5 spectrometer. ^1H and ^{13}C NMR spectra were determined with Varian XL-300 and Bruker AC-F-400 spectrometers. ESR spectra were obtained on Varian E-Line Century Series X-Band and Bruker 300E ESR spectrometers. Cyclic voltammetry (CV) experiments were performed at 293 K under argon with a EG & G PAR 174 A voltammograph and were current resistance compensated.

(*Z*)/(*E*)-Tetrahydrothiophen-3-one Tosylhydrazone. Tetrahydrothiophen-3-one (35.4 g, 347 mmol) was added dropwise to a mechanically stirred boiling solution of (*p*-toluenesulfonyl)hydrazine (65.9 g, 357 mmol) in absolute ethanol (350 mL). The solution was stirred and heated at reflux for 4 h. After cooling to room temperature, the reaction mixture was filtered and the resulting solid washed with absolute ethanol until the washings became clear. The almost white solid (67.9 g, 73%) was characterized as a 1:1 mixture of (*Z*)- and (*E*)-1: mp 163–65 °C; ^1H NMR (80 MHz, $CDCl_3$) δ_H 7.98 (bs, 1H), 7.83 (d, 2H, J = 8.1 Hz), 7.31 (d, 2H, J = 8.1 Hz), 3.45 (s, 2H), 3.30 (s, 2H), 3.0–2.9 (m, 2H), 2.9–2.7 (m, 4H), 2.6–2.5 (m, 2H), 2.4 (s, 3H); ^{13}C NMR ($CDCl_3$) 163.2, 144.4, 135.2, 129.7, 128.0, 37.1, 36.1, 30.3, 29.4, 29.3, 28.4, 21.6; IR (KBr) 3220, 1590, 1420, 1400, 1335, 1292, 1180, 1165, 1090, 1040, 920, 805, 660, 605, 555 cm^{-1}; UV (CH_3CN) λ_{max} nm (log ϵ) 229 (4.1), 193 (4.6); MS m/e (%) 270 (M^+, 30), 91 (C_7H_7, 100). Anal. Calcd for $C_{11}H_{14}N_2O_2S_2$: C, 48.4; H, 5.2; N, 10.4; S, 23.7. Found: C, 48.5; H, 5.4; N, 10.2; S, 23.5.

5,6-Dihydrothieno[3,2-*d*]-1,2,3-thiadiazole (2) and 4,6-Dihydrothieno[3,4-*d*]-1,2,3-thiadiazole (3). Thionyl chloride (62 mL, 825 mmol) was added cautiously at 0 °C over tosylhy-

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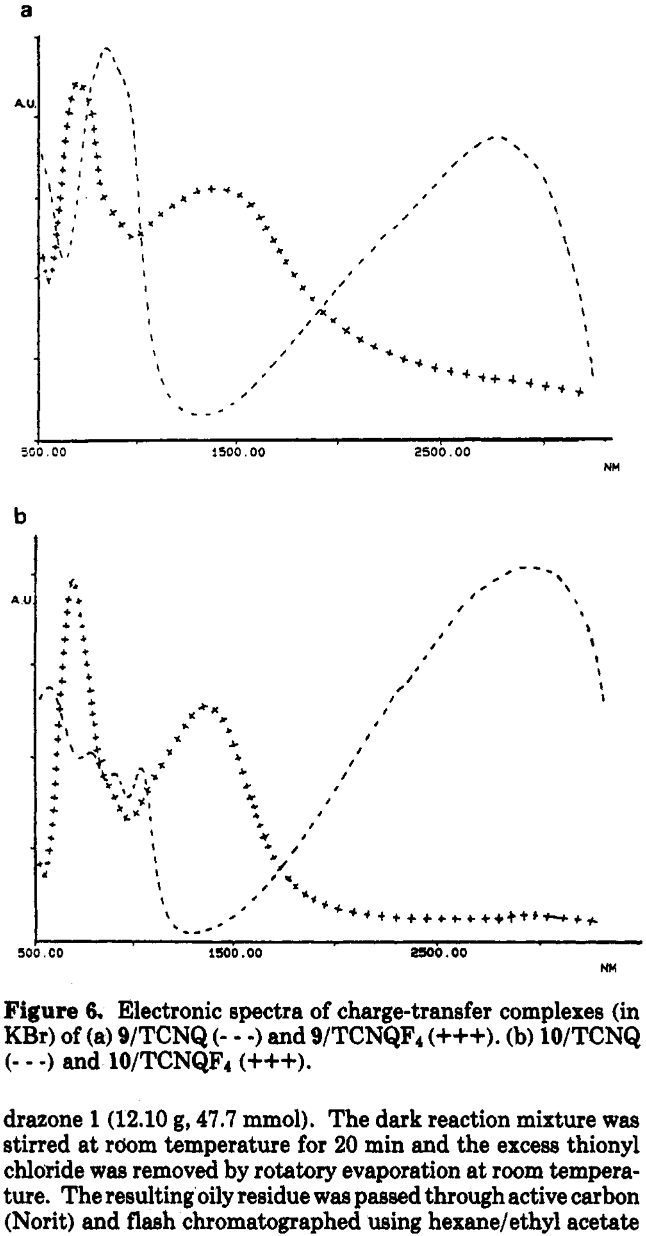

Figure 6. Electronic spectra of charge-transfer complexes (in KBr) of (a) **9**/TCNQ (- - -) and **9**/TCNQF$_4$ (+++). (b) **10**/TCNQ (- - -) and **10**/TCNQF$_4$ (+++).

drazone **1** (12.10 g, 47.7 mmol). The dark reaction mixture was stirred at room temperature for 20 min and the excess thionyl chloride was removed by rotatory evaporation at room temperature. The resulting oily residue was passed through active carbon (Norit) and flash chromatographed using hexane/ethyl acetate (3:1 v/v) as eluent. First was eluted a mixture of thiadiazoles, and second, pure thiadiazole **2** (1.181 g). Further flash chromatography of the first-eluted fraction (eluent initially hexane/ethyl acetate, 3:1 v/v, followed by dichloromethane) yielded thieno[3,2-*d*]-1,2,3-thiadiazole (**4**)(0.130 g), thiadiazole **3** (0.916 g), and thiadiazole **2** (0.690 g) as white solids.

Compound 2: 29%, mp 56–57 °C (ethyl ether–hexane); ^{1}H NMR (80 MHz, CDCl$_3$) δ_H 4.13(m, 2H), 3.52 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$) 168.1, 154.5, 42.8, 26.6; IR (KBr) 2940, 2840, 1435, 1425, 1360, 1248, 1195, 1125, 1100, 1012, 980, 955, 840, 789, 665, 520, 490 cm^{-1}; UV (CH$_3$CN) λ_{max} nm (log ϵ) 314 (3.9), 239 (3.3), 194 (3.8); MS *m/e* (%) 144 (M$^+$, 100). Anal. Calcd for $C_4H_4N_2S_2$: C, 33.3; H, 2.8; N, 19.4; S, 44.5. Found: C, 33.2; H, 2.8; N, 19.6; S, 44.7.

Compound 3: 14%, mp 86–89 °C (diethyl ether–hexane); ^{1}H NMR (80 MHz, CDCl$_3$) δ_H 4.41 (m, 2H) 4.25 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$) 169.8, 153.2, 28.5, 28.1; IR (KBr) 2940, 2920, 2845, 1505, 1440, 1265, 1260, 1095, 1010, 868, 840, 730, 690, 545, 518 cm^{-1}; UV (CH$_3$CN) λ_{max} nm (log ϵ) 291(2.8), 256 (3.2), 215 (3.6); MS *m/e* (%) 144 (M$^+$, 39.4), 70 (M$^+$ – CH_2N_2S, 100). Anal. Calcd for $C_4H_4N_2S_2$: C, 33.3; H, 2.8; N, 19.4; S, 44.5. Found: C, 33.3; H, 2.6; N, 19.2; S, 44.6.

Compound 4: 2%, mp 35–37 °C (hexane) (lit.[29] mp 32 °C); ^{1}H NMR (80 MHz, CDCl$_3$): δ_H 7.7, 7.1 (ABq, 2H, J = 6.4 Hz); ^{13}C NMR (100.6 MHz, CDCl$_3$) 170.9, 145.8, 42.8, 26.6; IR (KBr) 3110, 3090, 1430, 1265, 1240, 1120, 1080, 1030, 845, 770, 730, 665, 470 cm^{-1}; MS *m/e* (%) 142 (M$^+$, 28), 69 (M$^+$ – CHN_2S, 100). Anal. Calcd for $C_4H_2N_2S_2$: C, 33.8; H, 1.4; N, 19.7; S, 45.1. Found: C, 34.0; H, 1.4; N, 19.6; S, 45.3.

5,6-Dihydrothieno[2,3-*d*]-1,3-dithiole-2-thione (5). A solution of thiadiazole **3** (2.40 g, 16.6 mmol) in carbon disulfide (40 mL) was placed in a glass pressure vessel of 220 mL and heated to 190 °C for 4 days. After cooling, the reaction mixture was evaporated and the brown residue flash chromatographed (eluent CCl$_4$, 1:1 CCl$_4$–CHCl$_3$ → 1:10 CCl$_4$–CHCl$_3$) to yield (elution order) thieno[2,3-*d*]-1,3-dithiole-2-thione (**7**) as an amber solid (0.05 g, 1.5%), mp 125–126 °C (CCl$_4$–hexane) (lit.[7a] mp 125–125.5 °C); compound **5** as a yellow solid (2.34 g, 73%) mp 112–113 °C (CCl$_4$–hexane) (lit.[7b] mp 110–111 °C), and recovered compound **2** (0.25 g, 10.5%).

Compound 5: ^{13}C NMR (100.6 MHz, CDCl$_3$) 215.8, 135.2, 131.6, 37.2, 33.6; UV (CH$_3$CN) λ_{max} nm (log ϵ) 416 (4.0), 281 (3.6), 235 (3.9).

Compound 7: ^{13}C NMR (100.6 MHz, CDCl$_3$) 215.7, 138.5, 132.9, 130.8, 120.2; UV (CH$_3$CN) λ_{max} nm (log ϵ) 391 (4.2), 287 (3.7), 252 (3.8), 199 (4.2).

4,6-Dihydrothieno[3,4-*d*]-1,3-dithiole-2-thione (6). A solution of thiadiazole **2** (0.62 g, 4.3 mmol) in carbon disulfide (20 mL) was placed in a stainless steel autoclave of 120 mL at a pressure of 17 atm (N$_2$) and heated to 230 °C for 22 h. After cooling, the reaction mixture was evaporated and the brown residue flash chromatographed (eluent CCl$_4$, 1:1 CCl$_4$–CHCl$_3$ → 1:10 CCl$_4$–CHCl$_3$) to yield (elution order) thieno[3,4,-*d*]-1,3-dithiole-2-thione (8) (0.11 g, 13%), compound **6** as a yellow solid (0.40 g, 49%), and unreacted compound **3** (0.20 g, 32%).

Compound 6: mp 131–134 °C (CCl$_4$–hexane); ^{1}H NMR (80 MHz, CDCl$_3$) δ_H 4.00(s, 4H); ^{13}C NMR (100.6 MHz, CDCl$_3$) 217.5, 138.3, 34.6; IR (KBr) 2920, 2900, 2820, 1575, 1425, 1240, 1230, 1150, 1130, 1080, 1048, 865, 840, 710, 500, 450 430 cm^{-1}; UV (CH$_3$CN) λ_{max} nm (log ϵ) 381 (4.1), 263 (3.3), 234 (2.9), 199 (4.2); MS *m/e* (%) 192 (M$^+$, 100). Anal. Calcd for $C_5H_4S_4$: C, 31.2; H, 2.1; S, 66.7. Found: C, 30.9; H, 2.0; S, 67.1.

Compound 8: mp 142–143 °C (CCl$_4$–hexane) (lit.[30] mp 142 °C); ^{1}H NMR (80 MHz, CDCl$_3$) δ_H 7.20 (s, 2H); ^{13}C NMR (100.6 MHz, CDCl$_3$) 218.8, 138.0, 113.4; IR (KBr) 3100, 3090, 1490, 1445, 1412, 1320, 1150, 1110, 1060, 865, 830, 755, 500, 470 cm^{-1}; UV (CH$_3$CN) λ_{max} nm (log ϵ) 381 (4.1), 263 (3.3), 234 (2.9), 199 (4.2); MS *m/e* (%) 192 (M$^+$, 100). Anal. Calcd for $C_5H_4S_4$: C, 31.2; H, 2.1; S, 66.7. Found: C, 30.9; H, 2.0; S, 67.1.

4,4′,6,6′-Tetrahydro-$\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole (10). Thione **6** (0.55 g, 2.9 mmol) was heated to reflux in an argon atmosphere in 12 mL of freshly distilled trimethyl phosphite. The solution was refluxed for 3 h, during which brown crystals precipitated. The mixture was cooled to room temperature, filtered, washed with EtO$_2$ (50 mL), and dried (vacuum) to yield compound **10** as bright brown microcrystals (0.18 g, 39%): mp 226–227 °C; ^{1}H NMR (400 MHz, DMSO) δ_H 3.79 (s, 8H); IR (KBr) 2900, 2830, 1440, 1230, 1130, 1060, 875, 760, 705, 630, 440 cm^{-1}; UV (CH$_3$CN) λ_{max} nm (log ϵ) 530 (2.3), 463 (2.6), 365 (3.3), 308 (4.1); MS *m/e* (%) 320 (M$^+$, 80), 69 (M$^+$ – $C_7H_7S_5$, 100). Anal. Calcd for $C_{10}H_8S_6$: C, 37.5; H, 2.5; S, 60.0. Found: C, 37.4; H, 2.4; S, 59.9.

(*E*)-5,5′,6,6′-Tetrahydro-$\Delta^{2,2'}$-bithieno[2,3-*d*]-1,3-dithiole (9). Thione **5** (0.83 g, 4.3 mmol) was heated to reflux in an argon atmosphere in 17.5 mL of freshly distilled trimethyl phosphite. The solution was refluxed for 3 h, during which time dark red crystals precipitated. The mixture was cooled to room temperature, filtered, washed with EtO$_2$ (50 mL), and dried (vacuum) to yield compound **9** as a dark red solid (0.16 g, 23%): mp 191–193 °C dec (PhCl) (lit.[7a] mp 195–196 °C); ^{1}H NMR (80 MHz, DMSO) δ_H 3.81 (m, 4H), 2.87 (m, 4H); ^{13}C NMR (100.6 MHz, CDCl$_3$) 126.1, 122.7, 38.4, 33.1; IR (KBr) 2940, 2905, 2840, 1460, 1290, 1115, 1005, 865, 760, 460 cm^{-1}; UV (CH$_3$CN) λ_{max} nm (log ϵ) 530 (3.6), 345 (2.6), 290 (4.1); MS *m/e* (%) 320 (M$^+$, 31), 58 (M$^+$ – $C_8H_6S_5$, 100). Anal. Calcd for $C_{10}H_8S_6$: C, 37.5; H, 2.5; S, 60.0. Found: C, 37.5; H, 2.5; S, 60.3.

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(*Z*)/(*E*)-$\Delta^{2,2'}$-Bithieno[2,3-*d*]-1,3-dithiole (11). Thione 7 (0.25 g, 1.3 mmol) was heated to reflux in an argon atmosphere in 4 mL of freshly distilled trimethyl phosphite. The solution was refluxed for 2.5 h. After refrigeration (0 °C), 0.015 g (7%) of crystalline 11 were obtained, mp 213–214 °C dec (lit.[7a] mp 214–215 °C); IR (KBr) 3100, 1485, 1395, 1340, 1173, 1080, 1055, 890, 753, 675, 555, 580, 450 cm^{-1}; UV (CH_3CN) λ_{max} nm (log ϵ) 490 (2.3), 379 (3.2), 329 (4.0), 297(4.1); MS *m/e* (%) 316 (M^+, 100).

$\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole (12). By coupling thione 8 following the same procedure, compound 12 was obtained as yellow crystals (31%), mp 263–265 °C dec (lit.[7c] mp 259–260 °C); UV (CH_3CN) λ_{max} nm (log ϵ) 449 (2.1), 313 (4.3); ^{13}C NMR (100.6 MHz, $CDCl_3$) 135.6, 112.2.

Radical Cations. The preparation of radical cations in solution from the neutral donors was performed by oxidation with aluminum trichloride in methylene chloride in an argon atmosphere under red light.

TCNQ and TCNQF$_4$ Complexes. The complexes were synthesized by mixing equimolar solutions of the donor and acceptor in 1,1,2-trichloroethane (for BTDM-TTF, 10) or chlorobenzene (for BET-TTF, 9). Immediately, a dark solution resulted, from which the analytically pure 1:1 complex separates almost quantitatively.

9/TCNQ: Vis-NIR λ_{max} nm, 2805, 973 (sh), 876; IR (KBr), C≡N str 2205 cm^{-1}; Anal. Calcd for $C_{22}H_{12}N_4S_6$: C, 50.3; H, 2.3; N, 10.7; S, 36.7. Found: C, 50.5; H, 2.3; N, 10.7; S, 36.5.

9/TCNQF$_4$: Vis-NIR λ_{max} nm, 1391, 764 (sh), 695; IR (KBr), C≡N str 2200 cm^{-1}; Anal. Calcd for $C_{22}H_8F_4N_4S_6$: C, 44.3; H, 1.3; N, 9.2; S, 32.2. Found: C, 44.2; H, 1.6; N, 9.3; S, 32.4.

10/TCNQ: Vis-NIR λ_{max} nm, 2926, 1010, 879, 758, 550; IR (KBr), C≡N str 2206 cm^{-1}; Anal. Calcd for $C_{22}H_{12}N_4S_6$: C, 50.3; H, 2.3; N, 10.7; S, 36.7. Found: C, 50.1; H, 2.3; N, 10.4; S, 37.0.

10/TCNQF$_4$: Vis-NIR λ_{max} nm, 1369, 692; IR (KBr) C≡N str 2201 cm^{-1}; Anal. Calcd for $C_{22}H_8F_4N_4S_6$: C, 44.3; H, 1.3; N, 9.2; S, 32.2. Found: C, 44.4; H, 1.3; N, 9.0; S, 32.3.

Single crystals of complex 10/TCNQ (1:1) were also obtained by the slow diffusion technique using a TCNQ/acetonitrile solution and 10/carbon disulfide solution.[27]

X-ray Diffraction Studies. Red single crystals of BET-TTF 9 and yellow single crystals of DT-TTF 12 were obtained from CS_2 solutions.[31a]

Crystal data for compound 9: $C_{10}H_8S_6$, MW = 320.6, triclinic, $P1$, $a = 6.367(2)$ Å, $b = 7.160(3)$ Å, $c = 7.690(2)$ Å, $\alpha = 99.35(2)°$, $\beta = 101.25(2)°$, $\gamma = 101.25(2)°$, $V = 300.2(2)$ Å^3, $D_c = 1.77$ g/cm^3, $Z = 1$, $F(000) = 164$, $\mu = 10.6$ cm^{-1}, $\lambda = 0.71069$ Å. An irregular prismatic (0.09 × 0.35 × 1.10 mm) red crystal was used for the analysis.

Crystal data for compound 12: $C_{10}H_4S_6$, MW = 316.5, monoclinic, $P2_1/a$, $a = 10.906(2)$ Å, $b = 3.991(1)$ Å, $c = 14.030(3)$ Å, $\beta = 110.82(1)°$, $V = 570.8(2)$ Å^3, $D_c = 1.84$ g/cm^3, $Z = 2$, $F(000) = 320$, $\mu = 10.6$ cm^{-1}, $\lambda = 0.71069$ Å. An irregular prismatic (0.04 × 0.11 × 1.11 mm) yellow crystal was used for the analysis.

Data Collection. Crystals were mounted in an Enraf-Nonius CAD4 diffractometer with graphite monochromator and Mo Kα radiation at $T = 294$ K. Unit cell parameters were known from a least-squares analysis of 25 reflections. In both cases, intensity data was collected by zig-zag ρ–2θ scan technique and no fluctuations in standard reflections (three, measured each hour for both of them[9] were observed (9, 0.91%; 12, 0.65%). The 2θ range of measured reflections was $2° \le 50°$ for 9 and $2° \le 60°$ for 12. The index range was $-7 \le h \le 7$, $-8 \le k \le 8$, $0 \le l \le 19$ and $-15 \le h \le 15$, $-5 \le k \le 5$, $0 \le l \le 19$, respectively. For compound 9, 1196 reflections were collected, 1060 were unique reflections, and 1502 were considered to be observed ($F > \sigma(F)$) and used in the structure analysis; for compound 12, 3634 reflections were collected, 1603 were unique reflections, and 1502 were considered to be observed ($F > \sigma(F)$) and used in the structure analysis. In both cases, L_p corrections was applied, but no corrections for absorption were done.

Structure Refinements. The structures were solved by the following: 9, direct methods with a straigforward run of the MULTAN 11/84 program;[31b] 12, Patterson search methods with a run of the ROTSEARCH program.[32] In both cases a diagonal-matrix refinement on F was carried out with SHELX76 least-squares program,[33] using anisotropic thermal parameters for the non H-atoms and one global isotropic temperature factor for the H-atoms. The H-atoms were restrained at 1.08 Å from its carbon atoms for both molecules, for compound 9, S–C and C–C distances in the external ring were restrained at 1.75 and 1.52 Å, respectively. The refinement processes converged at $R = 0.058$, $R_w = 0.061$ with $\rho = 1/(\sigma^2(F) + 0.00054F^2)$ for compound 9 and at $R = 0.039$, $R_w = 0.047$ with $\rho = 1/(\sigma^2(F) + 0.000687F^2)$ for compound 12. Scattering factors were taken from *International Tables for X-ray Crystallography*,[34] except for those of the H-atoms.[35]

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