

15. An ESR Study of the Radical Cations of Tetrathiafulvalene (TTF) and Electron Donors Containing the TTF Moiety

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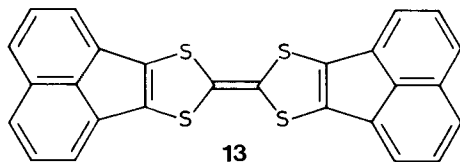
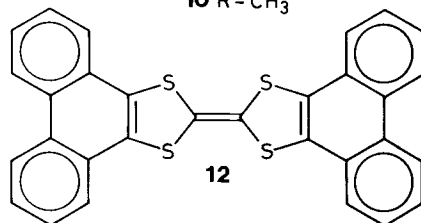
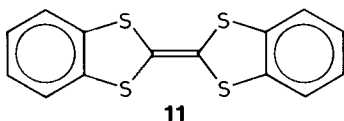
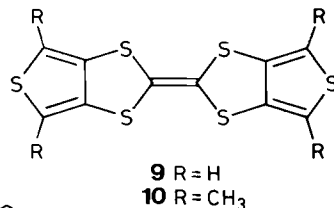
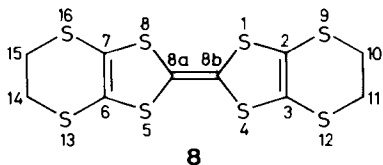
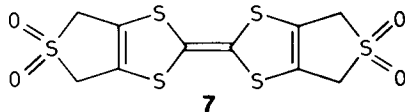
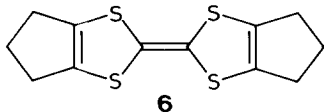
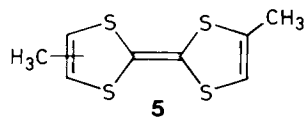
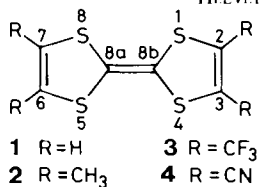
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Hyperfine data and g factors are reported for the radical cations of tetrathiafulvalene (TTF; **1**) and of its derivatives **2–13**. From the intense satellite spectra of $1^{\cdot+}$ – $13^{\cdot+}$ not only the coupling constants of the ^{33}S isotopes in the TTF moiety could be determined, but also, in favourable cases, those of the ^{13}C isotopes in the central double bond. The former values range from 0.370 (**8** $^{\cdot+}$) to 0.470 mT (**4** $^{\cdot+}$) and the latter from 0.255 (**8** $^{\cdot+}$) to 0.360 mT (**4** $^{\cdot+}$) in the radical cations of bis(ethylenedithio)-TTF (**8** $^{\cdot+}$) and tetracyano-TTF (**4** $^{\cdot+}$). The radical cation of TTF (**1** $^{\cdot+}$) exhibits intermediate values, 0.425 for the ^{33}S and 0.285 mT for the ^{13}C isotopes. The spin population in $1^{\cdot+}$ – $13^{\cdot+}$ resides, to a large extent, in the central $\text{S}_2\text{C} = \text{CS}_2$ part of the π -system. It tends to increase (decrease) by substitution with electron-accepting (donating) groups in the 2,3,6,7-positions of TTF.

Introduction. – Since the discovery of high electrical conductivity in the charge transfer complex of 1,4,5,8-tetrahydro-1,4,5,8-tetrathiafulvalene (TTF; 2-(1,3-dithiol-2-ylidene)-1,3-dithiole; **1**) and 7,8-tetracyanobenzo-1,4-quinodimethane (TCNQ) [1], a large number of such ‘organic metals’ have become known [2] [3]. Most of these superconducting materials are complexes or salts of electron donors structurally related to TTF. The spin distribution in the radical cations of the TTF-based donors is, therefore, of interest for understanding the properties of the pertinent ‘organic metals’.

Here, we describe the ESR studies on the radical cations of TTF (**1**) and of the following compounds derived from TTF by substitution or annelation in the 2,3,6,7-positions: tetramethyl-TTF (TM-TTF; 2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,5-dimethyl-1,3-dithiole; **2**), tetrakis(trifluoromethyl)-TTF (TTFM-TTF; 2-[4,5-bis(trifluoromethyl)-1,3-dithiol-2-ylidene]-4,5-bis(trifluoromethyl)-1,3-dithiole; **3**), tetracyano-TTF (TCN-TTF; 2-(4,5-dicyano-1,3-dithiol-2-ylidene)-1,3-dithiole-4,5-dicarbonitrile; **4**), a mixture (**5**) of 2,6- and 2,7-dimethyl-TTF (2,6- and 2,7-DM-TTF; (*E*)- and (*Z*)-2-(4-methyl-1,3-dithiol-2-ylidene)-4-methyl-1,3-dithiole), dicyclopenta-TTF (2-(5,6-dihydro-4*H*-cyclopenta-1,3-dithiol-2-ylidene)-5,6-dihydro-4*H*-cyclopenta-1,3-dithiole; **6**), bis(dioxothia-cyclopenta)-TTF (2-(4,6-dihydrothieno[3,4,-*d*]-1,3-dithiol-2-ylidene)-4,6-dihydrothieno[3,4-*d*]-1,3-dithiole-*S,S*,5,5-tetraoxide; **7**), bis(ethylenedithio)-TTF (BEDT-TTF; 2-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin; **8**), dithiopheno-TTF (2-thieno[3,4-*d*]-1,3-dithiol-2-ylidenethieno[3,4-*d*]-1,3-dithiole; **9**), bis(dimethylthiopheno)-TTF (2-(4,6-dimethylthieno[3,4-*d*]-1,3-dithiol-2-ylidene)-4,6-dimethylthieno[3,4-*d*]-1,3-dithiole; **10**), dibenzo-TTF (DB-TTF; 2-(1,3-benzodithiol-2-ylidene)-1,3-benzodithiole; **11**), bis(phenanthro-9,10)-TTF (2-phenanthro[9,10-*d*]-1,3-dithiol-2-ylidenephenanthro[9,10-*d*]-1,3-dithiole; **12**), and bis(acenaphtho-1,2)-TTF (8-acenaphtho[1,2-*d*][1,3]dithiol-8-ylideneacenaphtho[1,2-*d*][1,3]dithiole; **13**).



Some of the data given here for **1**⁺–**5**⁺ and **11**⁺ have been reported partly by other authors: **1**⁺ [4–10], **2**⁺ [6] [9] [10], **3**⁺ and **4**⁺ [10], **5**⁺ [6], and **11**⁺ [5] [8]. In those cases, we believe that our values are more precise and more reliable.

Experimental. – *Syntheses.* TTF (**1**) and BEDT-TTF (**8**) were purchased from *Strem Chemical Company* and used without further purification.

The alkyl derivatives of TTF, **2**, **5**, and **6**, were synthesized by treatment of the corresponding 1,3-dithiolium salts with trialkylamine [11] [12], which, in turn, were obtained from the appropriate α -bromoketones and potassium *o*-alkyl-dithiocarbonates (the 'xanthate route') [12–14].

TTFM-TTF (**3**) was prepared in one-step synthesis from hexafluoro-2-butyne and carbon disulfide, as described by *Hartzler* [15], while trimethylphosphite-induced coupling [16] of the corresponding 1,3-dithiole-2-thione [17] yielded TCN-TTF (**4**).

Compound **7** was produced by trimethylphosphite-induced coupling of the appropriate selenone which, in turn, was obtained in a multi-step synthesis from 3,4-dichlorothioliolane and the Na salt of *N,N*-dialkyl-dithiocarbamate [18].

Dithiothiopheno-TTF (**9**) was prepared by trimethylphosphite-induced coupling of the appropriate thione [19] which was obtained from 3,4-dibromothiophene by a modified procedure based on those described in [19] [20]. The tetramethyl derivative **10** was the product of triphenylphosphine-induced coupling of the corresponding dithiol-2-selone [21].

DB-TTF (**11**) was synthesized by coupling of the appropriate thione which was obtained in one step from thermal decomposition of benzothiadiazole in the presence of carbon disulfide [22].

Syntheses of both **12** and **13** started with treatment of the respective α -bromoketone with dithiocarbamate. This reaction was followed by an acid-induced ring closure, conversion to the corresponding 1,3-dithiole-1-thione (the 'carbamate route'), and coupling *via* the 1,3-dithiolium salt, as for **2**, **5**, and **6** [23].

Generation of the Radical Cations. The compounds 1–3 and 5–13 were oxidized to their radical cations with AlCl_3 or with $\text{CF}_3\text{COOH}/(\text{CF}_3\text{CO})_2\text{O}$ in H_2CCl_2 . A 1:1:10 mixture of $\text{CF}_3\text{COOH}/(\text{CF}_3\text{CO})_2\text{O}/\text{H}_2\text{CCl}_2$ served also as the solvent for an electrolytic oxidation of 4 to its radical cation. (The cell used for this oxidation has been described in [24]). The ESR spectra of the persistent radical cations 1^+ – 13^+ thus generated were taken in the temp. range of 193 to 293 K. Application of the ENDOR technique proved rather problematic, presumably because of unfavourable relaxation times. For the same reason, the hyperfine lines in the ESR spectra had larger widths (peak-to-peak distance ΔB_{pp} of 0.015–0.020 mT) than usually encountered with organic radicals (0.005–0.010 mT). Whereas the coupling constants did not markedly depend on the temperature, the ^{13}C and, in particular, the ^{33}S satellite lines exhibited a pronounced temp.-dependent hyperfine anisotropy.

Instrumental. The apparatus used was a Varian-E9-ESR Spectrometer with an attached Varian-ENDOR-1700 System. For a few selected radical cations, the g factors were determined with a Hewlett-Packard Microwavemeter and an NMR-Gaussmeter constructed in the Laboratorium für Physikalische Chemie der ETH Zürich¹⁾. The values obtained for these radical cations served as a reference for the remaining ones.

Results. – All radical cations 1^+ – 13^+ yielded intense satellite spectra from which the coupling constants of naturally abundant ^{33}S isotopes were readily and precisely determined. In several favourable cases, satellite lines arising from radical cations with ^{13}C isotopes in natural abundance could also be detected. The Table summarizes these ^{33}S and ^{13}C coupling constants, together with the g factors and the hyperfine data derived from the main spectra for the ^1H , ^{14}N , and ^{19}F nuclei. A more detailed report on the ESR studies is given below for each of the radical cations 1^+ – 13^+ . Wherever corresponding values have previously been published, a comparison is made with the data acquired in the present work.

TTF (1). Fig. 1 shows the well-known five-line ESR spectrum of 1^+ , along with its very intense satellite spectrum observed upon amplification of the signals. Within the limits of experimental error, the coupling constant of the four ring protons

Table. Hyperfine Coupling Constants a_X (in mT) and g Factors for the Radical Cations of 1–13

	X			g
	$^1\text{H}, ^{19}\text{F}, ^{14}\text{N}$	^{33}S	^{13}C	
1^+	0.125 (4H)	0.425 (4S)	0.285 (2C)	2.0081
2^+	0.074 (12H)	0.395 (4S)	a)	2.0078
3^+	0.067 (12F)	0.465 (4S)	a)	2.0079
4^+	0.012 (4N)	0.470 (4S)	0.360 (2C)	2.0080
5^+	0.132 (2H)	0.435 (2S)	a)	2.0079
	0.066 (6H)	0.390 (2S)		
6^+	0.211 (8H)	0.420 (4S)	a)	2.0078
	≤ 0.010 (4H)			
7^+	0.158 (8H)	0.425 (4S)	a)	2.0077
8^+	≤ 0.005 (8H)	0.370 (4S)	0.255 (2C)	2.0074
		≤ 0.080 (4S)		
9^+	0.020 (4H)	0.405 (4S)	a)	2.0077
10^+	≤ 0.005 (12H)	0.390 (4S)	0.355 (2C)	2.0076
11^+	0.049 (4H)	0.410 (4S)		2.0077
	0.015 (4H)			
12^+	0.028 (4H)	0.385 (4S)	a)	2.0074
13^+	0.017 (4H)	0.390 (4S)	0.26 ^{b)} (2C)	2.0073

a) Not observed. b) Estimated.

¹⁾ We thank Dr. A. Schweiger for making the instruments available to us.

($a_H = 0.125 \pm 0.002$ mT) agrees with the values (0.122 to 0.126 mT) reported in the literature [4–10], as does the ^{33}S coupling constant ($a_S = 0.425 \pm 0.005$ mT) when compared to the published values (0.42 to 0.427 mT) [7–10]. Moreover, we have succeeded in determining a hitherto unnoticed ^{13}C coupling constant ($a_C = 0.285 \pm 0.005$ mT) which has been assigned to ^{13}C isotopes in the two C-sites of the central double bond (positions 8a and 8b), by virtue of the relative intensity of the pertinent satellite lines (Fig. 1). The g factor (2.0081 ± 0.0001), measured for 1^+ in the present work, is equal to the value quoted in [8] [10], but it is somewhat lower than those (2.00838 and 2.0084) reported in [4] [6] [9].

2,3,6,7-Tetramethyl-TTF (2). The coupling constant of the twelve CH_3 protons in 2^+ ($a_H = 0.074 \pm 0.002$ mT) and the g factor of this radical cation (2.0078 ± 0.0001) match the values listed in [6] [10], which are significantly lower than those ($a_H = 0.078$ mT and

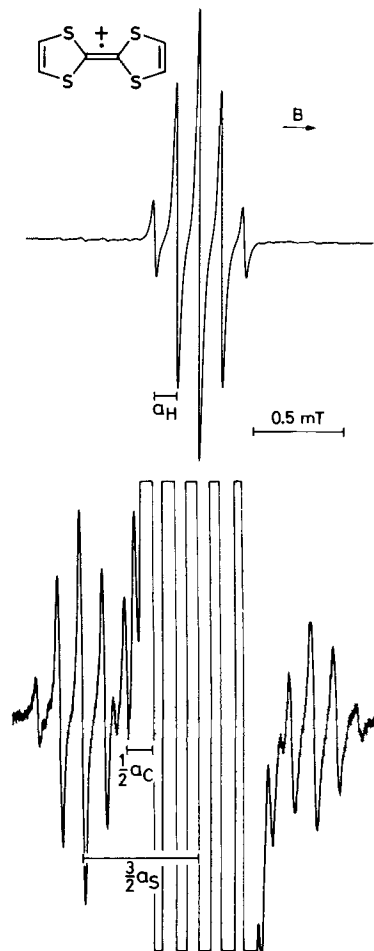


Fig. 1. ESR spectrum of 1^+ (top) and its amplification (bottom). Solvent: CH_2Cl_2 ; temp.: 233 K.

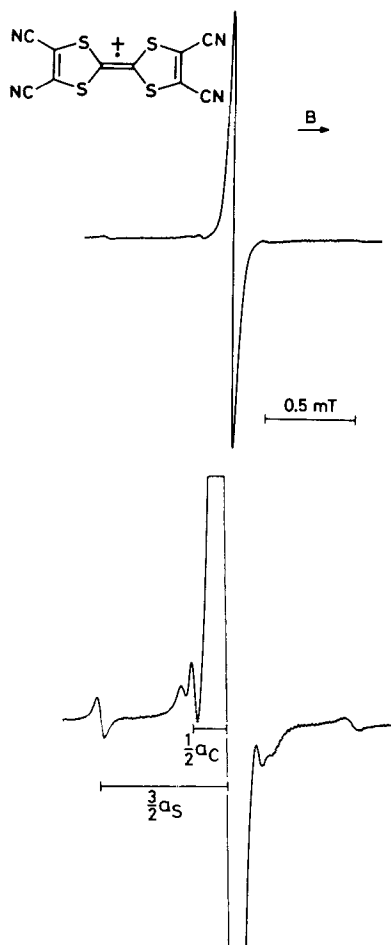


Fig. 2. ESR spectrum of 4^+ (top) and its amplification (bottom). Solvent: CH_2Cl_2 ; temp.: 253 K.

$g = 2.0081$) given in [9]. On the other hand, the ^{33}S coupling constant ($a_{\text{S}} = 0.395 \pm 0.005$) determined in the present work agrees with that (0.399 mT) reported in [9], while it considerably exceeds the corresponding value (0.33 mT) in [10].

2,3,6,7-Tetrakis(trifluoromethyl)-TTF (3). To our knowledge, the hyperfine data and the g factor of $\mathbf{3}^{\cdot+}$ have only quite recently been reported [10]. The spectral resolution obtained by those authors was much lower than the one achieved presently. Contrary to the coupling constant of the twelve ^{19}F nuclei, which does not significantly differ in the two studies ($a_{\text{F}} = 0.067 \pm 0.002$ mT, as compared with 0.069 mT in [10]), the ^{33}S coupling constant ($a_{\text{S}} = 0.465 \pm 0.005$ mT) and the g factor (2.0079 ± 0.0001) determined in this work are substantially larger than their counterparts ($a_{\text{S}} = 0.433$ mT and $g = 2.0070$) in [10].

2,3,6,7-Tetracyano-TTF (4). Due to the four strongly electron-attracting CN substituents, the compound $\mathbf{4}$ is much harder to oxidize than the other TTF derivatives dealt with in the present paper. The observation of an unresolved broad ESR signal (width 0.3 mT) upon reaction of $\mathbf{4}$ with SbCl_5 in CH_2Cl_2 was recently reported [10]. In our investigation, electrolysis of $\mathbf{4}$ (see *Experimental*) leads to the radical cation $\mathbf{4}^{\cdot+}$ which gives rise to the ESR spectrum shown in *Fig. 2*. From the main signal, of 0.05 mT width, the unresolved hyperfine splitting due to the four ^{14}N nuclei ($a_{\text{N}} = 0.012 \pm 0.002$ mT) can be derived by computer simulation, while the satellite spectrum (*Fig. 2*) readily yields the hitherto unreported ^{33}S and ^{13}C coupling constants ($a_{\text{S}} = 0.470 \pm 0.005$ and $a_{\text{C}} = 0.360 \pm 0.005$ mT); the latter value has been assigned to ^{13}C isotopes in the two C-sites of the central double bond, by analogy with the radical cation of the parent TTF ($\mathbf{1}$). The g factor (2.0080 ± 0.0001) of $\mathbf{4}^{\cdot+}$ is slightly higher than that (2.0077) of the broad signal obtained previously [10].

Mixture (5) of 2,6- and 2,7-Dimethyl-TTF. The ESR spectrum observed upon oxidation of $\mathbf{5}$ has been analyzed in terms of a single radical cation with the coupling constants due to two ring ($a_{\text{H}} = 0.132 \pm 0.004$ mT) and six CH_3 protons ($a_{\text{H}} = 0.066 \pm 0.004$ mT). Two coupling constants ($a_{\text{S}} = 0.435 \pm 0.005$ and 0.390 ± 0.005 mT), each arising from ^{33}S isotopes in two S-sites, are clearly evident. The a_{H} values and the g factor compare favourably with the data ($a_{\text{H}} = 0.128$ and 0.064 mT for two and six protons, respectively, and $g = 2.0079$) which have previously [6] been attributed to the radical cation of the single 2,6-isomer (see *Discussion*).

Dicyclopenta-TTF (6) and Bis(dioxothiacyclopenta)-TTF (7). A prominent feature in the so far not investigated ESR spectra of the radical cations $\mathbf{6}^{\cdot+}$ and $\mathbf{7}^{\cdot+}$ is the substantial coupling constant of the eight protons in the two CH_2 groups adjacent to the TTF moiety ($\mathbf{6}^{\cdot+}$: $a_{\text{H}} = 0.211 \pm 0.002$ mT; $\mathbf{7}^{\cdot+}$: $a_{\text{H}} = 0.158 \pm 0.002$ mT). The hyperfine splittings from the protons in the third, more removed CH_2 group of $\mathbf{6}^{\cdot+}$ is too small to be resolved ($a_{\text{H}} \leq 0.010$ mT). Within the limits of experimental error, the coupling constants assigned to ^{33}S isotopes in the four S-sites of the TTF moiety and the g factors are equal for both radical cations ($\mathbf{6}^{\cdot+}$: $a_{\text{S}} = 0.420 \pm 0.005$ mT and $g = 2.0078 \pm 0.0001$; $\mathbf{7}^{\cdot+}$: $a_{\text{S}} = 0.425 \pm 0.005$ mT and $g = 2.0077 \pm 0.0001$).

Bis(ethylenedithio)-TTF (8). This TTF derivative has recently become a favourite electron donor in 'organic metals' [3]. The ESR spectrum of its very persistent radical cation, $\mathbf{8}^{\cdot+}$, which has not yet been described in the literature, can be amplified to display not only the satellite lines of the 'first generation' (due to species with either *one* ^{33}S or *one*

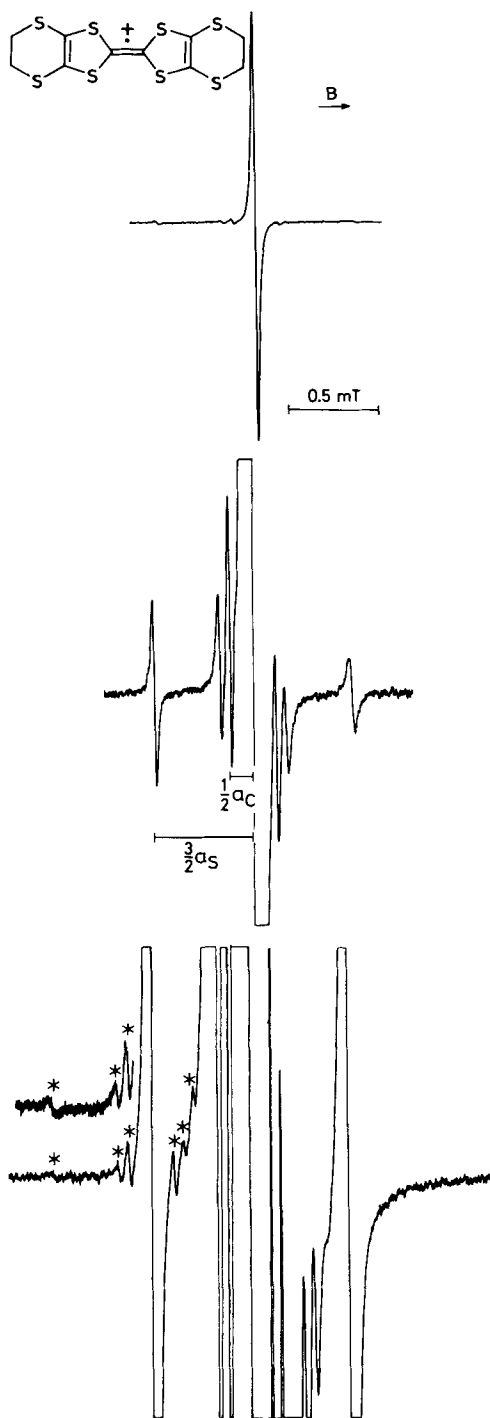


Fig. 3. ESR spectrum of 8^+ (top) and its moderate (middle) and strong amplification (bottom). Solvent: CH_2Cl_2 ; temp.: 233 K. The satellite lines of the 'second generation' are marked by asterisks.

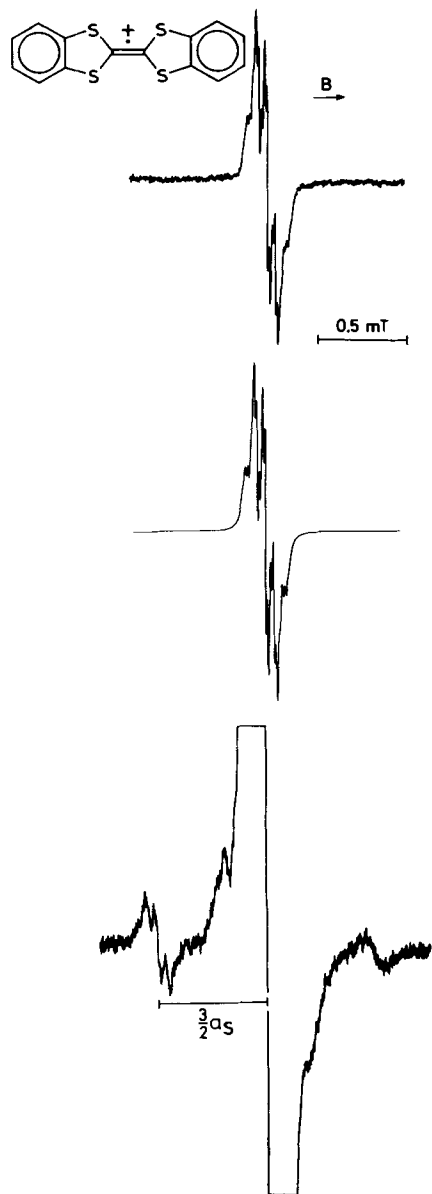


Fig. 4. ESR spectrum of 11^+ (top), its computer simulation (middle), and its amplification (bottom). Solvent: CH_2Cl_2 ; temp.: 233 K. The simulation made use of the coupling constants 0.049 and 0.015 mT, each from four protons.

^{13}C isotope), but also those of the 'second generation' (arising from species with *two* ^{33}S or *two* ^{13}C isotopes or *one* ^{33}S and *one* ^{13}C isotope) [25]. The effect of gradually increasing the amplification in the ESR spectrum of $\mathbf{8}^{\ddagger}$ is demonstrated in Fig. 3. Since the hyperfine splitting from the eight CH_2 protons ($a_{\text{H}} \leq 0.005$ mT) is too small to be resolved, the non-amplified spectrum consists of a single signal with a width ΔB_{pp} of 0.02 mT. From the satellite lines of the 'first generation', which already appear upon a moderate amplification, ^{33}S and ^{13}C coupling constants ($a_{\text{S}} = 0.370 \pm 0.005$ and $a_{\text{C}} = 0.255 \pm 0.005$ mT) are easily determined. By analogy with other radical cations in this series (Table), these values have been assigned to the ^{33}S and ^{13}C isotopes in the four S-sites of the TTF moiety and the two C-sites in its central double bond, respectively. An upper limit of 0.08 mT can be set to the coupling constant of the ^{33}S isotopes in the four S-sites outside the TTF moiety of $\mathbf{8}^{\ddagger}$. Further amplification of the signals reveals satellite lines of the 'second generation' at the low-field end of the spectrum. (Those at the high-field end are broadened beyond recognition due to the ^{33}S and ^{13}C hyperfine anisotropies; Fig. 3.) The g factor (2.0074 ± 0.0001) of $\mathbf{8}^{\ddagger}$ is markedly lower than that of $\mathbf{1}^{\ddagger}$.

Dithieno-TTF (9) and its Tetramethyl Derivative (10). ESR spectra of the radical cations of both **9** and **10** have not yet been reported. Whereas the coupling constant of the four ring protons in $\mathbf{9}^{\ddagger}$ ($a_{\text{H}} = 0.020 \pm 0.001$ mT) is still observable, the hyperfine splitting from the twelve CH_3 protons in $\mathbf{10}^{\ddagger}$ is too small to be resolved ($a_{\text{H}} \leq 0.005$ mT). The coupling constants, assigned to the ^{33}S isotopes in the four S-sites of the TTF moiety, and the g factors are similar for the two radical cations ($\mathbf{9}^{\ddagger}$: $a_{\text{S}} = 0.405 \pm 0.005$ mT and $g = 2.0077 \pm 0.0001$; $\mathbf{10}^{\ddagger}$: $a_{\text{S}} = 0.390 \pm 0.005$ mT and $g = 2.0076 \pm 0.0001$). In the case of $\mathbf{10}^{\ddagger}$, a ^{13}C coupling constant ($a_{\text{C}} = 0.355 \pm 0.005$ mT) is also apparent; their assignment to ^{13}C isotopes in the two C-sites of the central double bond seems indicated.

Dibenzo-TTF (11). Of the published reports [5] [8] on the ESR spectrum of $\mathbf{11}^{\ddagger}$, the first one [5] quotes the correct proton coupling constants which were determined with the application of the ENDOR technique (*cf.* Footnote 46 in [5]). However, the ESR spectrum, reproduced in Fig. 8 of [5], does not arise from $\mathbf{11}^{\ddagger}$, and that is why it 'could not be satisfactorily simulated with the ENDOR values', as stated in [5]. In the ESR spectrum of $\mathbf{11}^{\ddagger}$ reproduced in the second paper [8], the proton hyperfine splittings are unresolved. A highly resolved spectrum of $\mathbf{11}^{\ddagger}$ is shown in Fig. 4, along with its computer simulation which makes use of two coupling constants, each from a set of four protons ($a_{\text{H}} = 0.049 \pm 0.001$ and 0.015 ± 0.001 mT). In view of the small magnitude of these values, their assignments to individual sets of equivalent protons in the benzene rings are uncertain. From the satellite spectrum, likewise displayed in Fig. 4, the ^{33}S coupling constant ($a_{\text{S}} = 0.410 \pm 0.005$ mT) is derived in a straightforward way. It does not differ significantly from the a_{S} value (0.413 mT) quoted in [8]. The g factors measured in the present work (2.0077 ± 0.0001) and in [8] are equal.

Bis(phenanthro-9,10)-TTF (12) and Bis(acenaphtho-1,2)-TTF (13). The hitherto unknown radical cations of **12** and **13** contain four and three sets of four equivalent ring protons, respectively. Hyperfine splittings from only one set for either radical cation ($\mathbf{12}^{\ddagger}$: $a_{\text{H}} = 0.028 \pm 0.001$; $\mathbf{13}^{\ddagger}$: $a_{\text{H}} = 0.017 \pm 0.002$ mT) are partially resolved. Assignments of these coupling constants to protons in the specific positions of the phenanthrene ($\mathbf{12}^{\ddagger}$) or acenaphthylene moieties ($\mathbf{13}^{\ddagger}$) are difficult, considering the small magnitude of these values. The two radical cations exhibit essentially the same ^{33}S coupling constants and g factors ($\mathbf{12}^{\ddagger}$: $a_{\text{S}} = 0.385 \pm 0.005$ mT and $g = 2.0074 \pm 0.0001$; $\mathbf{13}^{\ddagger}$: $a_{\text{S}} = 0.390 \pm 0.005$ mT

and $g = 2.0073 \pm 0.0001$). In the case of $\mathbf{13}^{\ddagger}$, there is an indication of further satellite lines which presumably stem from ^{13}C isotopes in the two C-sites of the central double bond ($a_{\text{C}} = 0.26 \pm 0.03$ mT).

Discussion. - *Spin Distribution.* An HMO model, which makes use of the well-tried parameters $\alpha_{\text{S}} = \alpha + \beta$ and $\beta_{\text{CS}} = 0.7\beta$ [25] [26] has been applied to the radical cation of TTF (**1**). After correction by the *McLachlan* [27] procedure with $\lambda = 1.2$, it yields the π -spin populations $\rho_1 = 0.128$ at an S-atom, and $\rho_2 = 0.034$ and $\rho_{8a} = 0.174$ at a C-atom in the peripheral and central double bonds, respectively. These theoretical values can be tested against their experimental counterparts which are derived from the observed ^{33}S and proton coupling constants ($a_{\text{S}} = 0.425$ and $a_{\text{H}} = 0.125$ mT) by means of the relationships

$$a_{\text{S}} = Q_{\text{S}}\rho_1 \quad [25] [28] \quad (1)$$

$$a_{\text{H}} = Q_{\text{CH}}\rho_2 \quad [29] \quad (2)$$

and

$$4\rho_1 + 4\rho_2 + 2\rho_{8a} = 1. \quad (3)$$

Taking $Q_{\text{S}} = 3.3$ and $Q_{\text{CH}} = 2.9$ mT as parameters appropriate for radical cations, one obtains $\rho_1 = 0.129$, $\rho_2 = 0.043$, and $\rho_{8a} = 0.156$ for the 'experimental' π -spin populations in $\mathbf{1}^{\ddagger}$. Agreement with the simple theory is excellent for ρ_1 ; it is satisfactory for ρ_2 and ρ_{8a} .

The ^{13}C coupling constant ($a_{\text{C}} = 0.285$ mT) found for a C-site (8a) in the central double bond is related to the π -spin populations at this site (ρ_{8a}) and at the adjacent C- and S-atoms (ρ_5 , ρ_8 , and ρ_{8b}) by the equation [25] [30]

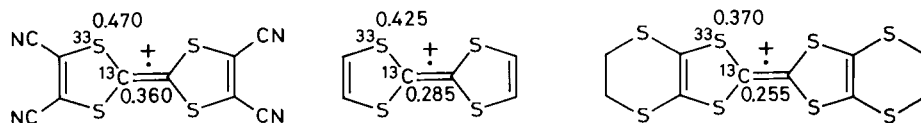
$$a_{\text{C}} = Q_{\text{C}}\rho_{8a} + Q_{\text{CC}}\rho_{8b} + Q_{\text{SC}}(\rho_5 + \rho_8). \quad (4)$$

Since $\rho_{8b} = \rho_{8a}$ and $\rho_5 = \rho_8 = \rho_1$, this equation is simplified to

$$a_{\text{C}} = (Q_{\text{C}} + Q_{\text{CC}})\rho_{8a} + 2Q_{\text{SC}}\rho_1. \quad (4a)$$

By use of the experimental spin populations $\rho_{8a} = 0.156$ and $\rho_1 = 0.129$, one can thus reproduce the value of the observed coupling constant a_{C} by setting the sum $Q_{\text{C}} + Q_{\text{CC}}$ to $(3.86 - 1.16)$ mT = 2.7 mT (as suggested in [31]) and by adopting -0.5_3 mT for Q_{SC} (instead of the previously proposed -0.8 mT [25]).

Accordingly, the bulk of the spin population in $\mathbf{1}^{\ddagger}$ resides in the $\text{S}_2\text{C} = \text{CS}_2$ part of the π system, as has been pointed out in [7] [10]. A similar spin distribution, with the unpaired electron largely confined to this partial π system, is also indicated for the radical cations of **2-13**. Thereby, electron-accepting substituents in the 2,3,6,7-positions of TTF increase the spin population in this π fragment, whereas electron-donating groups decrease it. Such a tendency is reflected by the ^{33}S and ^{13}C coupling constants for the radical cations of tetracyano-TTF (**4**) and bis(ethylenedithio)-TTF (**8**) as compared with the analogous values for the radical cation of the parent TTF (**1**).

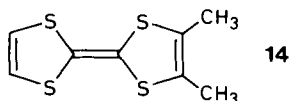


Coupling constants in mT

An HMO-*McLachlan* calculation for $\mathbf{8}^{\ddagger}$, analogous to that performed on $\mathbf{1}^{\ddagger}$, ($\alpha_s = \alpha + \beta$; $\beta_{CS} = \beta$; $\lambda = 1.2$) leads to the corresponding π -spin populations in the TTF moiety: $\rho_1 = 0.109$, $\rho_2 = 0.062$, and $\rho_{8a} = 0.128$; additionally, $\rho_9 = 0.015$ is obtained as the π -spin population at an outer S-atom. The theoretical ρ_1 value again agrees excellently with its experimental counterpart, $\rho_1 = 0.111$, as determined from the observed ^{33}S coupling constant ($a_s = 0.370$ mT) by means of *Eqn. 1* with $Q = 3.3$ mT. Although, unlike $\mathbf{1}^{\ddagger}$, the remaining experimental π -spin populations, ρ_2 , ρ_{8a} , and ρ_9 , cannot be derived in a straightforward way from the hyperfine data, an indirect test of theory against experiment is nevertheless possible. Thus, applying *Eqn. 4a* to $\rho_1 = 0.111$ (which is virtually identical by theory and experiment) and to the theoretical value $\rho_{8a} = 0.128$ with $Q_C + Q_{CC} = 2.7$ mT and $Q_{SC} = -0.5_3$ mT, one predicts a coupling constant $a_C = 0.230$ mT for a ^{13}C isotope in a C-site (C(8a)) of the central double bond. This result compares favourably with the experimental finding ($a_C = 0.255$ mT). Moreover, *Eqn. 1*, in which ρ_1 is replaced by the theoretical spin population $\rho_9 = 0.015$ ($Q_S = 3.3$ mT), yields the coupling constant $a_s = 0.050$ mT for a ^{33}S isotope in an outer S-site. This value lies below the upper limit derived for the pertinent coupling constant ($a_s \leq 0.08$ mT) from the ESR spectrum of $\mathbf{8}^{\ddagger}$. The rather low π -spin population ρ_9 at an outer S-atom is also consistent with the fact that the hyperfine splitting from the protons in a CH_2 group adjacent to such an atom is vanishingly small ($a_H \leq 0.005$ mT). The ratio $\rho_9:\rho_1 = 0.015:0.111 \approx 1:7$, indicated in the present work for the outer relative to the inner S-atoms in $\mathbf{8}^{\ddagger}$, contradicts the result of a CNDO calculation recently reported in [32] that such a ratio should be *ca.* 1:2.

The high π -spin population at the four S-atoms in the TTF moiety of $\mathbf{1}^{\ddagger}$ - $\mathbf{13}^{\ddagger}$ is responsible for the enlarged line-widths in the ESR spectra, the strong ^{33}S anisotropy and the enhanced g factors.

Methyl Substitution. Examination of the proton coupling constants for the radical cations of TTF ($\mathbf{1}$), 2,3,6,7-tetramethyl-TTF ($\mathbf{2}$), 2,3-dimethyl-TTF (2-(1,3-dithiol-2-ylidene)-4,5-dimethyl-1,3-dithiole; $\mathbf{14}$) [6], and a mixture ($\mathbf{5}$) of 2,6- and 2,7-dimethyl-TTF calls for two comments.



i) The coupling constants (a_H in mT) of both ring ($\mathbf{1}^{\ddagger}$: 0.125; $\mathbf{14}^{\ddagger}$: 0.118; $\mathbf{5}^{\ddagger}$: 0.132) and CH_3 protons ($\mathbf{2}^{\ddagger}$: 0.074; $\mathbf{14}^{\ddagger}$: 0.082; $\mathbf{5}^{\ddagger}$: 0.066) are not very sensitive to the position and number of the CH_3 substituents. Thus, for all radical cations, replacement of a ring H-atom by a CH_3 group results in a change in the absolute a_H value from 0.125 ± 0.007 to 0.074 ± 0.008 mT, where 0.007 and 0.008 mT is the range of deviation from the values for $\mathbf{1}^{\ddagger}$, and $\mathbf{2}^{\ddagger}$, respectively. It is, therefore, possible that the isomeric radical cations of the experimentally inseparable 2,6- and 2,7-dimethyl-TTF exhibit similar and, within the limits of the achieved resolution, indistinguishable proton coupling constants. This means that the ESR spectrum, which is observed upon oxidation of a mixture ($\mathbf{5}$) of the two dimethyl-TTF's and which appears to arise from a single radical cation (see *Results*), can, in fact, be due to both isomeric species. Such an interpretation represents a viable alternative to that proposed previously in terms of only one radical cation (of 2,6-dimethyl-TTF) [6]. It is also noteworthy that the two coupling constants a_s , each due to ^{33}S

isotopes in two S-sites of 5^{\ddagger} , are very close to the corresponding values for the ^{33}S isotopes in the four S-sites of 1^{\ddagger} and 2^{\ddagger} : (5^{\ddagger} : 0.435 and 0.390 mT; 1^{\ddagger} : 0.425 mT; 2^{\ddagger} : 0.395 mT).

ii) The marked decrease in the (absolute) a_{H} value on going from the ring protons in 1^{\ddagger} , 14^{\ddagger} , and 5^{\ddagger} to the CH_3 protons in 2^{\ddagger} , 14^{\ddagger} , and 5^{\ddagger} is itself remarkable. It contrasts with the usual finding for the radical cations that the coupling constants of the protons in the CH_3 substituents (β -protons) are larger than those of the ring protons (α -protons) in the corresponding positions of the parent π system [33] [34]. The 'anomalous' behaviour of the radical cations in the TTF series has also been noticed by other authors [10]. The reasons for it are unclear. Particularly, since the coupling constant of the CH_2 protons ($a_{\text{H}} = 0.211$ mT), determined in the present work for the radical cation of dicyclopenta-TTF (**6**), must be considered as 'normal'. Allowing for the \cos^2 -dependence of this β -proton coupling constant [34] [35], one derives a hypothetical a_{H} value of *ca.* 0.14 mT = $0.211 \text{ mT} / (2\cos^2 30^\circ)$ for the protons in a freely rotating CH_3 group. Such a value is in full accord with expectation.

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