Oxidation of phosphines containing two or three tetrathiafulvalene (TTF) or *o*-dimethyl-TTF moieties. Evidence for formation of radical polycations

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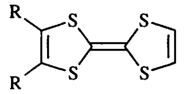
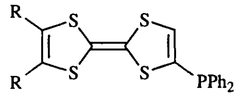
Stepwise oxidation of tetrathiafulvalenyl(diphenyl)phosphine (1), 4′,5′-dimethyltetrathiafulvalen-4-yl(diphenyl)phosphine (1a), bis(tetrathiafulvalenyl)phenylphosphine (2), bis(4′,5′-dimethyltetrathiafulvalen-4-yl)phenylphosphine (2a), tris(tetrathiafulvalenyl)phosphine (3) and tris(4′,5′-dimethyltetrathiafulvalen-4-yl)phosphine (3a) was followed by EPR and ENDOR spectroscopy, and cyclic voltammetry. Each of the tetrathiafulvalene (TTF) or 4,5-dimethyltetrathiafulvalene (*o*-DMTTF) moieties in 1–3a donates two electrons, so that exhaustive oxidation at potentials below 1 V (*vs.* SCE) leads to the dications 1^{2+} or $1a^{2+}$, the tetracations 2^{4+} or $2a^{4+}$ and the hexacations 3^{6+} or $3a^{6+}$. In 2, 2a, 3 and 3a, the electrons are removed one-by-one from different TTF or *o*-DMTTF moieties. In the initially formed radical cations $2^{\cdot+}$, $2a^{\cdot+}$, $3^{\cdot+}$ and $3a^{\cdot+}$, the electron hole is delocalized over all TTF or *o*-DMTTF moieties, two in $2^{\cdot+}$ or $2a^{\cdot+}$ and three in $3^{\cdot+}$ or $3a^{\cdot+}$. On the other hand, in paramagnetic species produced by further oxidation and also giving rise to well defined EPR and ENDOR spectra, the unpaired electron appears on the hyperfine time-scale as localized in only one donor moiety. These species are supposed to be the radical trications $2^{\cdot 3+}$ or $2a^{\cdot 3+}$ and the radical pentacations $3^{\cdot 5+}$ or $3a^{\cdot 5+}$. The intermediately occurring dications 2^{2+} or $2a^{2+}$ and 3^{2+} or $3a^{2+}$, as well as the tetracations 3^{4+} or $3a^{4+}$, should have a triplet ground-state, while the trications 3^{3+} or $3a^{3+}$ are expected to be quartet species.

In contrast to numerous radical trianions which have been studied by EPR spectroscopy for *ca.* 15 years,[1] there have been hardly any reports on analogous investigations of monoradicals bearing three or more positive charges.[2] To our knowledge, papers in this field deal exclusively with triplet dications[3–5] and/or quartet trications.[4–7] Appropriate candidates for the generation of polycations are molecules containing two or more donor moieties with a relatively weak interaction. Tetrathiafulvalene (TTF) and its derivatives represent the most popular donor π-systems and they have been used for the last two decades in conducting and superconducting radical cation salts.[8a] While the first materials based on TTF and tetramethyltetraselenafulvalene (TMTSeF) were described as highly one-dimensional, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts exhibit two-dimensional arrangements from both the geometrical and electronic point of view.[8b] Thus, extended or non-planar molecules with increased potential for two- or three-dimensional interactions have been devised, *e.g.* by linking two or three TTF or 4,5-dimethyltetrathiafulvalene (*o*-DMTTF) moieties in a non-planar arrangement as in bis(tetrathiafulvalenyl)phenylphosphine (**2**), bis(4′,5′-dimethyltetrathiafulvalen-4-yl)phenylphosphine (**2a**), tris(tetrathiafulvalenyl)phosphine (**3**) and tris(4′,5′-dimethyltetrathiafulvalen-4-yl)phosphine (**3a**).[9–11] These phosphines, like 1,2-bis(4′,5′-dimethyltetrathiafulvalen-4-yl)ethane[12] and molecules in which two TTF or *o*-DMTTF moieties are fused to 1,4-ditellurin,[13] meet the requirement for weakly interacting donor moieties.

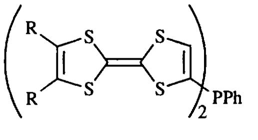
Here we describe the oxidation products of **2**, **2a**, **3** and **3a**; those of the structurally related tetrathiafulvalenyl(diphenyl)phosphine (**1**) and 4′,5′-dimethyltetrathiafulvalen-4-yl-(diphenyl)phosphine (**1a**) are also included for comparison. The radical cations $\mathbf{1}^{\cdot+}$, $\mathbf{1a}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, $\mathbf{2a}^{\cdot+}$, $\mathbf{3}^{\cdot+}$ and $\mathbf{3a}^{\cdot+}$, as well as the multiply oxidized species which are supposed to be the radical polycations $\mathbf{2}^{\cdot 3+}$, $\mathbf{2a}^{\cdot 3+}$, $\mathbf{3}^{\cdot 5+}$ and $\mathbf{3a}^{\cdot 5+}$, have been characterized by their hyperfine data with the use of EPR and ENDOR spectroscopy.



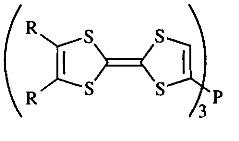
TTF R = H
o-DMTTF R = Me



1 R = H
1a R = Me



2 R = H
2a R = Me



3 R = H
3a R = Me

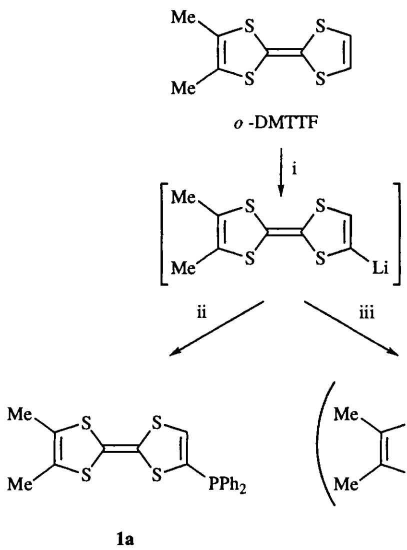
Results

Syntheses

The syntheses of **1**–**3**[9,10] and **2a**[11] have already been reported. **1a** and **3a** were synthesized in an analogous way from the lithium derivative of *o*-DMTTF and $PClPh_2$ or PBr_3 (see Scheme 1 and Experimental section).

EPR and ENDOR spectra

TTF, *o*-DMTTF and the phosphines **1**–**3a** were oxidized in CH_2Cl_2 to their radical cations either chemically with $AgClO_4$, $AlCl_3$ or CF_3COOH, or electrolytically on a helical gold anode with 0.1 M Bu_4NClO_4 as the supporting salt.[14] The EPR and ENDOR spectra were taken at 253–313 K, a range in which



Scheme 1 i, Pr$^i{}_2$NH, BuLi, −70 °C, Et$_2$O; ii, ClPPh$_2$; iii, 1/3 PBr$_3$

they did not significantly depend on temperature. The radical cations TTF$^{\bullet+}$ and *o*-DMTTF$^{\bullet+}$ were very persistent and their concentration decreased only slowly upon further oxidation to the diamagnetic dications TTF^{2+} and *o*-DMTTF^{2+}. The EPR spectra of **1**$^{\bullet+}$ and **1a**$^{\bullet+}$ are exemplified in Fig. 1 by that of **1**$^{\bullet+}$. They exhibit hyperfine interactions with the *three* protons in the TTF moiety of **1**$^{\bullet+}$ or the *seven* protons in the *o*-DMTTF moiety of **1a**$^{\bullet+}$ and also with the ^{31}P nucleus, while the protons of the phenyl substituents do not give rise to observable splittings. Unlike TTF$^{\bullet+}$ and *o*-DMTTF$^{\bullet+}$, the radical cations **1**$^{\bullet+}$ and **1a**$^{\bullet+}$ were not very persistent under the applied conditions, as they gradually converted into secondary paramagnetic species here denoted (**1**$^{\bullet+}$)′ and (**1a**$^{\bullet+}$)′. Fig. 1 also presents the EPR spectrum of (**1**$^{\bullet+}$)′ as an example. The interacting protons and the ^{31}P nucleus in (**1**$^{\bullet+}$)′ or (**1a**$^{\bullet+}$)′ seem to be the same as those in their forerunners **1**$^{\bullet+}$ or **1a**$^{\bullet+}$, but the ^{1}H and ^{31}P coupling constants, a_H and a_P, are significantly altered on going from the latter to the former. The major change occurs with the $|a_P|$ values which undergo a multiple increase upon this conversion. The structures of (**1**$^{\bullet+}$)′ and (**1a**$^{\bullet+}$)′ have not been established beyond doubt (see Discussion section).

The EPR spectra of **2**$^{\bullet+}$, **2a**$^{\bullet+}$, **3**$^{\bullet+}$ and **3a**$^{\bullet+}$, which generally were the first paramagnetic species detected upon oxidation of the corresponding phosphines, are represented by those of **2**$^{\bullet+}$ and **3**$^{\bullet+}$ in Fig. 2. Their hyperfine patterns stem from an interaction with the protons of *all* TTF or *o*-DMTTF moieties and the ^{31}P nucleus; splittings from the phenyl protons in **2**$^{\bullet+}$ and **2a**$^{\bullet+}$ are again unresolved. Thus, the number of interacting protons is *six* in **2**$^{\bullet+}$, *fourteen* in **2a**$^{\bullet+}$, *nine* in **3**$^{\bullet+}$ and *twenty-one* in **3a**$^{\bullet+}$. The coupling constants a_H for **2**$^{\bullet+}$ or **2a**$^{\bullet+}$ amount to roughly half the corresponding values for **1**$^{\bullet+}$ or **1a**$^{\bullet+}$, while those for **3**$^{\bullet+}$ or **3a**$^{\bullet+}$ are approximately one-third of these values. The EPR spectra of **2**$^{\bullet+}$, **2a**$^{\bullet+}$, **3**$^{\bullet+}$ and **3a**$^{\bullet+}$ disappeared upon further oxidation, whereby unresolved absorptions of *ca.* 8 mT width were revealed with the use of enhanced modulation. These absorptions became more intense on lowering the temperature, but attempts to resolve them did not meet with success even at 20 K. When the oxidation process was prolonged, new well defined EPR spectra emerged. Their hyperfine patterns resemble those of **1**$^{\bullet+}$ (Fig. 1) or **1a**$^{\bullet+}$, the interaction being restricted to the protons of only *one* TTF or *o*-DMTTF moiety and to the ^{31}P nucleus. These spectra are attributed to the radical trications **2**$^{\bullet3+}$ or **2a**$^{\bullet3+}$ and to the radical pentacations **3**$^{\bullet5+}$ or **3a**$^{\bullet5+}$ (see Discussion section). As in the case of **1**$^{\bullet+}$ or **1a**$^{\bullet+}$, they were gradually replaced by the spectra of secondary paramagnetic species (**2**$^{\bullet3+}$)′ or (**2a**$^{\bullet3+}$)′ and (**3**$^{\bullet5+}$)′ or (**3a**$^{\bullet5+}$)′, with somewhat different coupling constants a_H and strikingly enlarged $|a_P|$ values. Such modifications of the hyperfine patterns on going from primary to secondary radical polycations parallel those observed upon formation of (**1**$^{\bullet+}$)′ (Fig. 1) or (**1a**$^{\bullet+}$)′ from their forerunners, thus pointing to analogous structural changes.

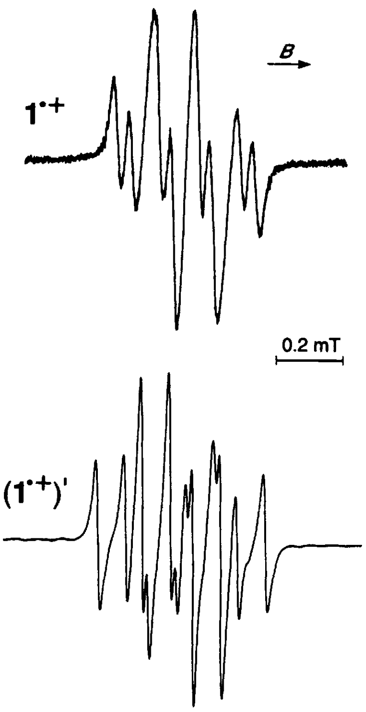


Fig. 1 EPR spectra of **1**$^{\bullet+}$ and (**1**$^{\bullet+}$)′; solvent, CH$_2$Cl$_2$; counterion, ClO$_4^-$; temperature, 293 K

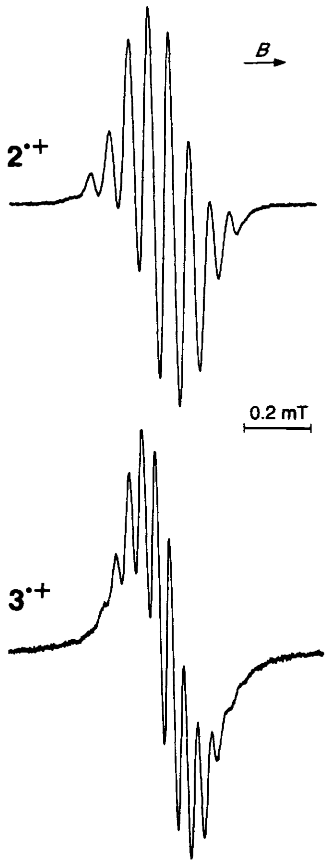


Fig. 2 EPR spectra of **2**$^{\bullet+}$ and **3**$^{\bullet+}$; solvent, CH$_2$Cl$_2$; counterion, ClO$_4^-$; temperature, 293 K

The course of reaction leading from the neutral molecules **2**, **2a**, **3** and **3a** to their radical polycations *via* the corresponding

Table 1 ^{1}H and ^{31}P coupling constants, a_H and a_P in mT,[a] for the radical cations and polycations of TTF, *o*-DMTTF and the phosphines **1**, **1a**, **2**, **2a**, **3** and **3a**

	a_H (α)	a_H (α)	a_P		a_H (α)	a_H (β)	a_P
TTF$^{\cdot+\,b}$	−0.125 (2 H)	−0.125 (2 H)		*o*-DMTTF$^{\cdot+\,b}$	−0.083 (2 H)	+0.130 (6 H)	
1$^{\cdot+\,b}$	−0.114 (1 H)	−0.126 (2 H)	−0.055 (1 P)	**1a**$^{\cdot+\,b}$	−0.088 (1 H)	+0.091 (6 H)	−0.035 (1 P)
(**1**$^{\cdot+}$)$'^{\,b}$	−0.081 (1 H)	−0.133 (2 H)	−0.156 (1 P)	(**1a**$^{\cdot+}$)$'^{\,b}$	−0.076 (1 H)	+0.095 (6 H)	−0.141 (1 P)
2$^{\cdot+\,b}$	−0.061 (2 H)	−0.061 (4 H)	−0.054 (1 P)	**2a**$^{\cdot+\,b}$	−0.045 (2 H)	+0.045 (12 H)	−0.034 (1 P)
2$^{\cdot3+\,c}$	−0.104 (1 H)	−0.129 (2 H)	−0.056 (1 P)	**2a**$^{\cdot3+\,c}$	−0.086 (1 H)	+0.092 (6 H)	−0.035 (1 P)
(**2**$^{\cdot3+}$)$'^{\,c}$	−0.070 (1 H)	−0.134 (2 H)	−0.164 (1 P)	(**2a**$^{\cdot3+}$)$'^{\,c}$	−0.058 (1 H)	+0.106 (6 H)	−0.159 (1 P)
3$^{\cdot+\,b}$	−0.039 (3 H)	−0.039 (6 H)	−0.070 (1 P)	**3a**$^{\cdot+\,b}$	−0.030 (3 H)	+0.030 (18 H)	−0.050 (1 P)
3$^{\cdot5+\,c}$	−0.090 (1 H)	−0.135 (2 H)	−0.025 (1 P)	**3a**$^{\cdot5+\,c}$	−0.085 (1 H)	+0.097 (6 H)	−0.023 (1 P)
(**3**$^{\cdot5+}$)$'^{\,c}$	−0.068 (1 H)	−0.140 (2 H)	−0.178 (1 P)	(**3a**$^{\cdot5+}$)$'^{\,c}$	−0.060 (1 H)	+0.105 (6 H)	−0.144 (1 P)

[a] Experimental error: ±0.002 mT. [b] Oxidation with $AgClO_4$. [c] Oxidation with CF_3COOH (*ca.* 30% per volume).

monocations depended on the oxidation method used. With $AgClO_4$ and by electrolysis, the progress of oxidation could readily be monitored, so that the spectra of the radical cations **2**$^{\cdot+}$, **2a**$^{\cdot+}$, **3**$^{\cdot+}$ and **3a**$^{\cdot+}$ were always observed prior to those of the more highly oxidized species. On the other hand, with $AlCl_3$ and CF_3COOH, care had to be taken not to push the oxidation too far and, thereby miss the formation of the monocations. When an excess of neutral phosphine, **2** or **2a**, was added to a solution showing the spectrum of the corresponding radical polycation, **2**$^{\cdot3+}$ or **2a**$^{\cdot3+}$ (generated with $AgClO_4$), the spectrum of the respective monocation reappeared, evidently due to oxidation of the neutral compound by its radical polycation.

The ^{1}H and ^{31}P hyperfine data, a_H and a_P, for all radical cations and polycations dealt with in the present work, are listed in Table 1. They depended slightly on the oxidation method used. The a_H values for TTF$^{\cdot+}$ and *o*-DMTTF$^{\cdot+}$ agree with those reported previously.[15,16] The analyses of the EPR spectra were corroborated by the ENDOR technique, as demonstrated for **2**$^{\cdot3+}$ and (**2**$^{\cdot3+}$)$'$ in Fig. 3. Signals from the ^{31}P nucleus are apparent there, along with those from the sets of one and two protons in one TTF moiety, while the protons in the second TTF moiety and in the phenyl substituent have coupling constants that are too small to give rise to observable signals. General TRIPLE-resonance experiments[17] carried out on the ENDOR signals indicated that the ^{31}P nucleus and the protons attached directly to the rings of the TTF or *o*-DMTTF moieties have coupling constants a_P and a_H of the same sign, which is opposite to that of the a_H values of the methyl protons. Such ring and methyl protons are usually denoted α and β, respectively. Theory requires negative coupling constants for the former and positive ones for the latter;[18a] the a_P values ought thus to be negative. For the radical cations **2**$^{\cdot+}$ or **2a**$^{\cdot+}$ and **3**$^{\cdot+}$ or **3a**$^{\cdot+}$, in which the electron hole is delocalized over all TTF or *o*-DMTTF moieties, the coupling constants $|a_H|$ were equal within the limits of experimental resolution. On the other hand, for **1**$^{\cdot+}$ or **1a**$^{\cdot+}$, **2**$^{\cdot3+}$ or **2a**$^{\cdot3+}$ and **3**$^{\cdot5+}$ or **3a**$^{\cdot5+}$, as well as for their secondary products (**1**$^{\cdot+}$)$'$–(**3a**$^{\cdot5+}$)$'$, *i.e.* for the radical cations and polycations with the unpaired electron localized on one TTF or *o*-DMTTF moiety, the $|a_H|$ values of one proton were smaller than those of the remaining two or six protons (Table 1). The single proton is readily identified with the one attached to the carbon atom neighbouring the C–P bond, in accord with simple MO calculations. For such radical cations and polycations with the 'localized' unpaired electron, satellite lines from ^{33}S isotopes in natural abundance were also observed. The ^{33}S coupling constants, a_S, lie in the range +0.42 to +0.45 mT, characteristic of radical cations of TTF and its derivatives.[16] The positive sign of these a_S values is in line with the larger widths of the satellite lines at the high-field relative to those at the low-field side of the spectrum.[18b] The *g* factor of all radical cations and polycations was 2.0080 ± 0.0003.

Electrochemistry

Table 2 lists the oxidation potentials of the phosphines **1**–**3a**, as determined by cyclic voltammetry in the previous[10,11] and present work; these data are compared with those for TTF or *o*-DMTTF. All values lie in two distinct potential regions which, for every compound, are separated by *ca.* 0.4 V. The cyclic voltammograms of **1** and **1a**, like those of TTF and of *o*-DMTTF, exhibited two reversible waves, *one* in each of the two potential regions. The number of such waves in the lower-potential region increased to *two* for **2** or **2a** and to *three* for **3** or **3a**. These waves were rather close to each other with a separation of *ca.* 0.1 V. A further, irreversible wave was observed in the higher-potential region; it involved transfer of *two* electrons for **2** or **2a** and of *three* for **3** or **3a**.

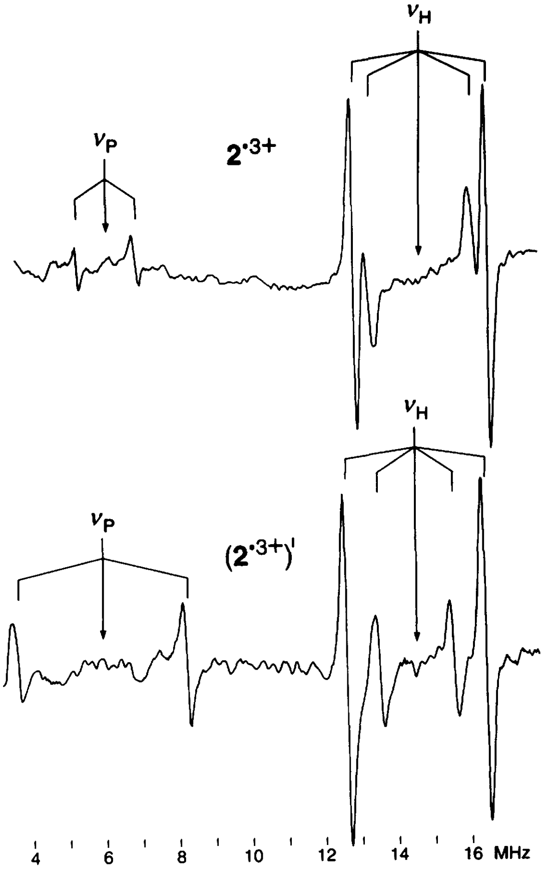


Fig. 3 ^{1}H and ^{31}P ENDOR spectra of **2**$^{\cdot3+}$ and (**2**$^{\cdot3+}$)$'$; solvent, CH_2Cl_2; counterion, CF_3COO^-; temperature, 233 K

In order to correlate the findings by EPR spectroscopy with the waves observed in the cyclic voltammograms, an electrolytic cell was constructed which allowed both studies on the same solutions to be carried out. This cell, of which the set-up followed the description in the literature,[19] contained working and counter-electrodes of platinum, the former terminating in a short helix. The reference electrode was silver wire coated with AgCl. The solvent (CH_2Cl_2) and the supporting salt (0.1 M

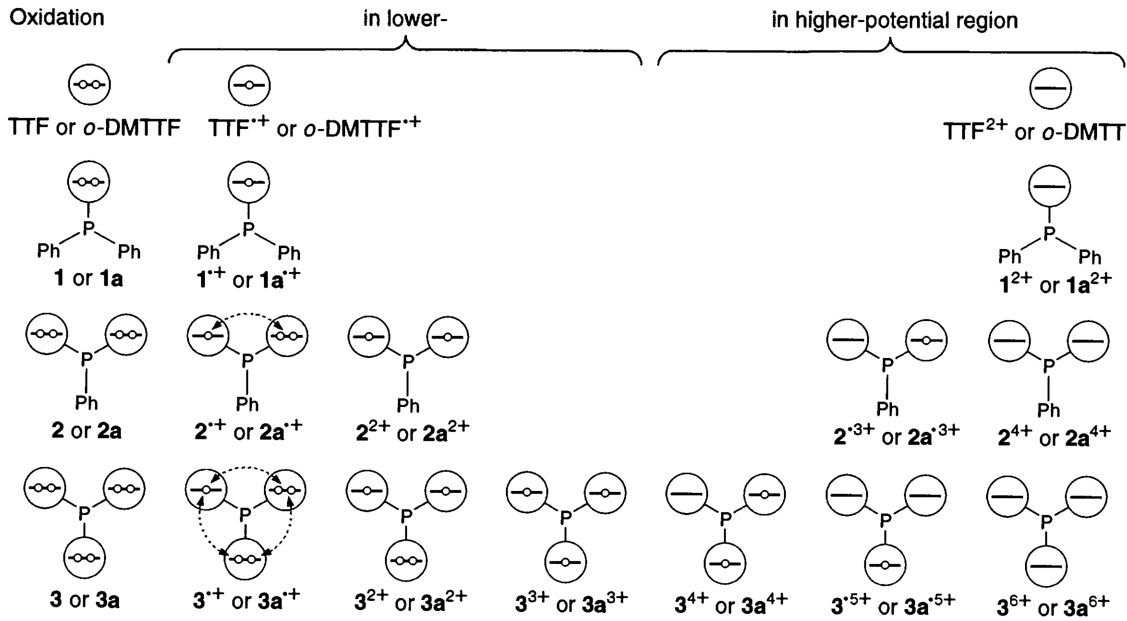


Fig. 4 Diagrams of the stepwise electron removal from TTF, *o*-DMTTF and the phosphines **1**, **1a**, **2**, **2a**, **3** and **3a**. The larger circles represent the TTF or *o*-DMTTF molecules or such moieties in the phosphines with their HOMOs.

Table 2 Half-wave oxidation potentials, $E_{1/2}$/V *vs.* SCE[a] for TTF, *o*-DMTTF and the phosphines **1**, **1a**, **2**, **2a**, **3** and **3a**

	Potential region	
	Lower	Higher
TTF	0.32	0.72
o-DMTTF	0.28	0.65
1	0.38	0.74
1a	0.32	0.70
2	0.37; 0.47	0.84[b,c]
2a	0.30; 0.40	0.82[b,c]
3	0.35; 0.47; 0.54	0.86[d,c]
3a	0.27; 0.38; 0.47	0.78[d,c]

[a] Experimental error: ±0.03 V; calibrated relative to ferrocene. [b] Two-electron wave. [c] Oxidation potential E_p; wave irreversible, because of precipitation at the electrode. [d] Three-electron wave.

Bu_4NClO_4) were the same as those used in electrolytical generation of radical cations for EPR studies and in cyclic voltammetry (see Experimental section). Apart from a systematic shift of the potentials relative to those measured with a conventional cell (Table 2), the waves in the two potential regions were generally reproducible. In the case of TTF, *o*-DMTTF, **1** and **1a**, assignments of the first wave in the lower-potential region to the formation of the radical cations $TTF^{\bullet+}$, *o*-$DMTTF^{\bullet+}$, $\mathbf{1}^{\bullet+}$ and $\mathbf{1a}^{\bullet+}$ and of the second one in the higher-potential region to their conversion into the dications TTF^{2+}, *o*-$DMTTF^{2+}$, $\mathbf{1}^{2+}$ and $\mathbf{1a}^{2+}$ are obvious. The first waves of **2**, **2a**, **3** and **3a**, also in the lower-potential region, occurred together with the EPR spectra attributed to the radical cations $\mathbf{2}^{\bullet+}$, $\mathbf{2a}^{\bullet+}$, $\mathbf{3}^{\bullet+}$ and $\mathbf{3a}^{\bullet+}$. Raising the potential led to the disappearance of these spectra, whereupon the broad unresolved EPR absorptions were observed. The latter attenuated on going into the higher-potential region, in which a further wave and associated new EPR spectra appeared. Of these spectra, merely those ascribed to the secondary species denoted $(\mathbf{2}^{\bullet3+})'$ and $(\mathbf{2a}^{\bullet3+})'$ could be disclosed with certainty. The failure to identify clearly the radical polycations $\mathbf{2}^{\bullet3+}$, $\mathbf{2a}^{\bullet3+}$, $\mathbf{3}^{\bullet5+}$ and $\mathbf{3a}^{\bullet5+}$ under these conditions will be discussed below.

Discussion

Fig. 4 depicts schematically the stepwise removal of electrons upon oxidation of TTF, *o*-DMTTF, **1**, **1a**, **2**, **2a**, **3** and **3a**. In the potential range below +1 V *vs.* SCE, the π-system of TTF or *o*-DMTTF donates two electrons which are consecutively removed from the HOMO, giving rise to the radical cations $TTF^{\bullet+}$ or *o*-$DMTTF^{\bullet+}$ and, subsequently, to the diamagnetic dications TTF^{2+} or *o*-$DMTTF^{2+}$. Electronic repulsion of the two positive charges originating from the partial vacation of the HOMO in the *same* TTF or *o*-DMTTF π-system is responsible for the difference of *ca.* 0.4 V between the potential of the first and the second oxidation wave, each in a separate region of the cyclic voltammogram. The electrochemical behaviour of **1** and **1a** closely resembles that of TTF and *o*-DMTTF, respectively. Evidently this behaviour is governed by the TTF or *o*-DMTTF moiety of **1** or **1a**, being largely independent of the rest of the molecule. It is hardly surprising that the presence of several TTF or *o*-DMTTF moieties has a dominating effect on the electrochemistry of **2**, **2a**, **3** and **3a**. The two oxidation waves of **2** and **2a** and the three such waves of **3** and **3a** occur in the lower-potential region. Their separation by *ca.* 0.1 V points to a relatively small electrostatic repulsion of the positive charges which must, therefore, be located one-by-one in *different* TTF or *o*-DMTTF moieties (Fig. 4). The species initially formed in the very first wave are the radical cations $\mathbf{2}^{\bullet+}$, $\mathbf{2a}^{\bullet+}$, $\mathbf{3}^{\bullet+}$ and $\mathbf{3a}^{\bullet+}$, wherein the exchange of the electron hole between the two or three spin-bearing moieties is fast on the hyperfine time-scale. The closely following waves in the same lower-potential region, namely one for **2** or **2a** and two for **3** or **3a**, are due to formation of the dications $\mathbf{2}^{2+}$ or $\mathbf{2a}^{2+}$ and $\mathbf{3}^{2+}$ or $\mathbf{3a}^{2+}$ and of the trications $\mathbf{3}^{3+}$ or $\mathbf{3a}^{3+}$ (see below). At this stage, the two TTF or *o*-DMTTF moieties of **2** or **2a** and the three such moieties of **3** or **3a** are all singly charged, so that additional electrons have to be donated by $\mathbf{2}^{2+}$ or $\mathbf{2a}^{2+}$ and $\mathbf{3}^{3+}$ or $\mathbf{3a}^{3+}$, in which each TTF or *o*-DMTTF π-system is already endowed with a positive charge. Consequently, further oxidation waves are now clearly separated from the preceding ones by *ca.* 0.4 V and appear in the higher-potential region. Coalescence of two waves for **2** or **2a** and of three for **3** or **3a** into one wave in this region signifies that electrons are consecutively removed from *different* TTF or *o*-DMTTF moieties at essentially the same potential, despite the progressively increased positive charges. For **2** or **2a**, the resulting products are the radical trications $\mathbf{2}^{\bullet3+}$ or $\mathbf{2a}^{\bullet3+}$ and the diamagnetic tetracations $\mathbf{2}^{4+}$ or $\mathbf{2a}^{4+}$, while, in the case of **3** or **3a**, continued oxidation yields the tetracations $\mathbf{3}^{4+}$ or $\mathbf{3a}^{4+}$, the radical pentacations $\mathbf{3}^{\bullet5+}$ or $\mathbf{3a}^{\bullet5+}$ and the diamagnetic hexacations $\mathbf{3}^{6+}$ or $\mathbf{3a}^{6+}$ (Fig. 4). Contrary to the corresponding radical monocations, the exchange of the unpaired electron between the TTF or *o*-DMTTF moieties in the radical polycations $\mathbf{2}^{\cdot 3+}$ or $\mathbf{2a}^{\cdot 3+}$ and $\mathbf{3}^{\cdot 5+}$ or $\mathbf{3a}^{\cdot 5+}$, is slow on the hyperfine time-scale. The intermediately formed species in the lower-potential region, the dications $\mathbf{2}^{2+}$ or $\mathbf{2a}^{2+}$ and $\mathbf{3}^{2+}$ or $\mathbf{3a}^{2+}$ and the trications $\mathbf{3}^{3+}$ or $\mathbf{3a}^{3+}$, as well as the tetracations $\mathbf{3}^{4+}$ or $\mathbf{3a}^{4+}$ produced in the higher-potential region, give rise presumably to the broad unresolved EPR absorptions observed between the disappearance of the EPR spectra of $\mathbf{2}^{\cdot +}$, $\mathbf{2a}^{\cdot +}$, $\mathbf{3}^{\cdot +}$ and $\mathbf{3a}^{\cdot +}$ and the emergence of such spectra of $\mathbf{2}^{\cdot 3+}$, $\mathbf{2a}^{\cdot 3+}$, $\mathbf{3}^{\cdot 5+}$ and $\mathbf{3a}^{\cdot 5+}$. The dications $\mathbf{2}^{2+}$, $\mathbf{2a}^{2+}$, $\mathbf{3}^{2+}$ and $\mathbf{3a}^{2+}$ and the tetracations $\mathbf{3}^{4+}$ and $\mathbf{3a}^{4+}$ are likely to have a triplet ground-state, while the trications $\mathbf{3}^{3+}$ and $\mathbf{3a}^{3+}$ should be quartet species. Theoretical calculations on structurally related molecules containing two or three equivalent donor moieties predict a triplet and quartet ground-state for the corresponding biradical dications and triradical trications, respectively.[3,7] Most relevant to the phosphines **2**–**3a** are such calculations on molecules, in which two TTF moieties are linked by a $>$C=X group, where X = CH_2, O, S or $C(CN)_2$.[3] In some cases, observation of EPR spectra of triplet dications and quartet trications exhibiting zero-field splittings has been reported.[5,6] Unfortunately, in the present work, only broad unresolved absorptions were apparent for the species in question, so that their spin multiplicities could not definitely be established. The total width (*ca.* 8 mT) of these absorptions is compatible with twice the zero-field splittings expected for two spin-bearing moieties separated by 800–900 pm.[20]

Although, with the electrolytic cell constructed for the present studies, the EPR spectra of $\mathbf{2}^{\cdot 3+}$ or $\mathbf{2a}^{\cdot 3+}$ associated with the oxidation waves in the higher-potential region were not directly observed, the appearance of those arising from the secondary products $(\mathbf{2}^{\cdot 3+})'$ or $(\mathbf{2a}^{\cdot 3+})'$ strongly suggest that the primary radical trications $\mathbf{2}^{\cdot 3+}$ or $\mathbf{2a}^{\cdot 3+}$ are also produced. The fact that, under these conditions, spectra of $\mathbf{3}^{\cdot 5+}$ or $\mathbf{3a}^{\cdot 5+}$ and $(\mathbf{3}^{\cdot 5+})'$ or $(\mathbf{3a}^{\cdot 5+})'$, which could unequivocally be identified as such, failed to be detected, may be due to the following: because $\mathbf{3}^{\cdot 5+}$ or $\mathbf{3a}^{\cdot 5+}$ are generated at essentially the same potential as $\mathbf{3}^{4+}$ or $\mathbf{3a}^{4+}$ and $\mathbf{3}^{6+}$ or $\mathbf{3a}^{6+}$, reactions such as $2 \times \mathbf{3}^{\cdot 5+}(\mathbf{3a}^{\cdot 5+}) \longrightarrow \mathbf{3}^{4+}(\mathbf{3a}^{4+}) + \mathbf{3}^{6+}(\mathbf{3a}^{6+}) \longrightarrow 2 \times \mathbf{3}^{6+}(\mathbf{3a}^{6+}) + 2e^-$ lead to a fast disappearance of the intermediate primary radical pentacations prior to their conversion to $(\mathbf{3}^{\cdot 5+})'$ or $(\mathbf{3a}^{\cdot 5+})'$.

The detailed molecular structure of the secondary radical cations or polycations $(\mathbf{1}^{\cdot +})'$, $(\mathbf{1a}^{\cdot +})'$, $(\mathbf{2}^{\cdot 3+})'$, $(\mathbf{2a}^{\cdot 3+})'$, $(\mathbf{3}^{\cdot 5+})'$ and $(\mathbf{3a}^{\cdot 5+})'$, formed from the corresponding primary species $\mathbf{1}^{\cdot +}$–$\mathbf{3a}^{\cdot 5+}$, is still open to discussion. Conversion of the latter into the former presumably occurs by a reaction at the central phosphorus atom which passes from the tri- to penta-valency by binding an additional atom or a group of atoms. Such a conversion was observed during electrocrystallization of trimethyltetrathiafulvalenyl(diphenyl)phosphine which reacted with traces of water to yield the corresponding phosphine oxide.[21] A structural change at the phosphorus atom is in line with the finding that the most substantial changes in the hyperfine data on going from the primary to the secondary radical cations of **1** or **1a** and the radical polycations of **2** or **2a** and **3** or **3a** are observed for the ^{31}P coupling constants. However, in the absence of additional hyperfine splittings, the nature of the atom or group of atoms becoming attached to the phosphorus atom remains unrevealed.

With respect to the electronic structure of all primary and secondary radical cations and polycations considered in the present work, it is noteworthy that the ^{31}P coupling constants are throughout relatively small and negative. This finding indicates that the phosphorus atom is situated in the nodal plane of the singly occupied orbitals which, therefore, represent antibonding combinations of the HOMOs of the TTF or *o*-DMTTF moieties.

Experimental

Materials

TTF was a commercial product of Fluka, Buchs. The syntheses of samples of **1**, **2** and **3**[9,10] as well as that of **2a**[11] were reported in previous work. The preparation of *o*-DMTTF, **1a** and **3a** is described below. All reactions were carried out under dry argon. Standard vacuum techniques were used while manipulating organolithium derivatives. The solvents THF and Et_2O were distilled from Na–Ph_2CO immediately before use.

***o*-DMTTF.** The original procedure[22] was modified as reported for other TTF-containing molecules.[23] Trimethyl phosphite (26 ml, 0.2 mol) was added to a solution of 1,3-dithiolium iodide (46 g, 0.2 mol) in CH_3CN (300 ml). A slightly exothermic reaction took place while the yellow colour of the dithiolium iodide disappeared. The solution was stirred for 1 h and the solvent was removed under vacuum. The remaining oil was dissolved in dry THF (500 ml) and transferred to a three-neck flask equipped with a mechanical stirrer. The solution was cooled to −70 °C and Bu^tOK (22.4 g, 0.2 mol) dissolved in dry THF (100 ml) was added over 30 min, followed by finely ground 1-(4,5-dimethyl-1,3-dithiol-2-yl)piperidinium hexafluorophosphate (72 g, 0.2 mol) which was added in one portion. The thick suspension was stirred for 1 h at −70 °C and then allowed to warm up to −10 °C over 1 h. After addition of Et_2O and filtration of the precipitated salts over Celite, the filtrate was concentrated under vacuum to *ca.* 100 ml, diluted with toluene (1 l) and treated dropwise with glacial acetic acid (45 ml) until the solution darkened. After stirring for 1 h, the solution was washed with water (3 x 250 ml), dried over $MgSO_4$ and concentrated. Filtration over SiO_2 (eluent, toluene) and recrystallization from CH_3CN afforded *o*-DMTTF as orange crystals (25.5 g, 55%), mp 116–118 °C (lit.,[15] 117–119 °C).

Compound 1a. To a solution of *o*-DMTTF (465 mg, 2 mmol) in dry Et_2O (20 ml) at −70 °C was added successively diisopropylamine (0.28 ml, 2 mmol) and BuLi (2.5 M in hexane, 0.8 ml, 2 mmol). After stirring at −70 °C for 2 h, the yellow suspension was treated dropwise with chloro(diphenyl)phosphine (0.36 ml, 0.44 g, 2 mmol). After warming up to room temp., the solvent was evaporated and the residue purified by flash chromatography (eluent, toluene). Recrystallization from AcOEt afforded **1a** as orange crystals (0.57 g, 68%), mp 128–130 °C [Calc. (found) for $C_{20}H_{17}S_4P$: C, 57.67 (57.72); H, 4.11 (4.14); S, 30.78 (30.37); P, 7.44% (7.31%)]; δ_H($CDCl_3$, Me_4Si) 7.46 (br s, 10 H), 6.70 (d, 1 H, J_{H-P} 9 Hz), 1.96 (s, 6 H); δ_P(CH_2Cl_2, H_3PO_4 85%) −13.4.

Compound 3a. To a solution of *o*-DMTTF (1.86 g, 8 mmol) in dry Et_2O was added successively at −70 °C diisopropylamine (1.12 ml, 8 mmol) and BuLi (1.8 M in hexane, 5 ml, 9 mmol) and the mixture was stirred for 1 h at −70 °C. To the yellow suspension was added dropwise phosphorus tribromide (0.19 ml, 0.541 g, 2 mmol) dissolved in Et_2O (10 ml). After stirring overnight at room temp., the solvent was evaporated and the solid residue Soxhlet-extracted with CH_2Cl_2. The yellow extract was further recrystallized from toluene to afford **3a** as orange needles (0.95 g, 49%), mp 232–234 °C [Calc. (found) for $C_{24}H_{21}S_{12}P$: C, 39.75 (39.71); H, 2.92 (2.81); S, 53.06 (52.69); P, 4.27% (4.32%)]; δ_H[$(CD_3)_2SO$, Me_4Si] 7.29 (d, 3 H, J_{H-P} 10.5 Hz), 1.94 (s, 18 H, Me); δ_P(CH_2Cl_2, H_3PO_4 85%) −33.06.

Instrumental

The instruments used for recording the ^1H and $^{31}P\{^1H\}$ NMR spectra were a JEOL-PMX60 at 60 MHz and a Bruker-AC200SY at 81.0 MHz, respectively. The EPR spectra were taken on a Varian-E9-instrument, while a Bruker-ESP-300-system served for the ENDOR and TRIPLE-resonance studies. The cyclic voltammograms were recorded on a PAR-273 potentiostat[10,11] or on a Metrohm Polarecord E506 equipped with a VA-stand 663 and VA-scanner E612. Working electrode, Pt disk; counter-electrode, Pt wire; solvent, CH_2Cl_2 or CH_3CN; supporting salt, 0.05 M Bu_4NPF_6[10,11] or 0.1 M Bu_4NClO_4; temperature, 298 K; scan, 100 mV s^{-1}.

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