

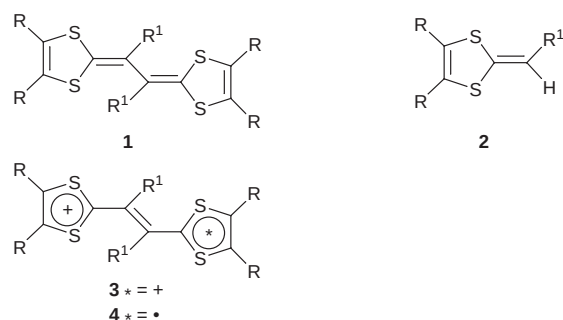
Synthesis and properties of novel tetrathiafulvalene vinylogues

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The cation radical states of novel TTF vinylogues with *o*-substituted phenyl groups at the vinyl positions are thermodynamically stable, and X-ray analyses of the cation radical salts have revealed the planar structures of the TTF vinylogue parts and unique crystal structures.

Tetrathiafulvalene (TTF) vinylogues **1** with extended π -conjugation are promising electron donors for organic



conductors due to their highly electron-donating properties and reduced on-site Coulombic repulsion.¹ The parent compound² and the ethylenedithio derivative³ were synthesized several years ago. Recently the derivatives of **1** containing substituents such as aryl groups at the vinyl positions have been prepared by several groups.⁴ They have been considered to be non-planar molecules due to the steric interactions between the substituents and the 1,3-dithiole parts, and X-ray analyses revealed the severely deformed structures.^{4c,d,e} Therefore, those TTF molecules have not been used as components for organic conductors. However, the TTF vinylogue skeletons can be planar when the aryl substituents are twisted away from the π -conjugated framework. These compounds are expected to afford conductors with unusual structures since good molecular overlapping is disturbed by the bulky substituents. We have now prepared various derivatives **1** by a convenient method and have found that the cation radicals of **1** containing *o*-substituted phenyl groups are thermodynamically stable and can be isolated as single crystals.

The derivatives of **1** were previously prepared by electrochemical oxidative coupling of the corresponding 1,4-dithiafulvenes **2**.^{4b,c,e,5} We have recently reported oxidative intramolecular cyclization to give bis(1,3-dithiole) electron donors by using tris(4-bromophenyl)aminium hexachloroantimonate as the oxidation reagent.⁶ We have now used this chemical oxidation for the synthesis of **1**. First, 1,4-dithiafulvene derivatives **2** were prepared by either Wittig reaction of a phosphonium salt (for the dibenzo derivatives) or Wittig–Horner reaction of a phosphonium ester (for the ethylenedithio derivatives) with the corresponding aldehydes. Reaction of **2** with the aminium salt in CH₂Cl₂ afforded dication salts **3** which are formed by oxidative dimerization followed by oxidation. The salts **3** were reduced with zinc in MeCN to give **1**. The yields of **1** from **2** were 20–85%. It is noteworthy that the naphthyl and pyrenyl derivatives as well as phenyl derivatives were prepared.

The oxidation potentials of the donors **1** (Table 1) were measured by cyclic voltammetry (CV). The methyl derivatives

1a,m and the phenyl ones **1b,n** show reversible one-stage two-electron redox waves. The *p*-substituted derivatives **1g,h,q** and the *m*-substituted one **1i** also undergo the similar two-electron oxidation. This fact suggests that the cation radical states of these compounds are thermodynamically unstable due to non-planar structures, similar to the reported examples. On the other hand, the *o*-substituted derivatives **1c–f,j,o,p,r** showed two reversible one-electron oxidation waves similar to the non-substituted one **1t**. This result suggests that the cation radicals of the *o*-substituted phenyl derivatives are thermodynamically stable. This can be explained by considering that the TTF vinylogue skeletons are planar when there are *o*-substituents, which increase the steric interactions and make the phenyl parts twist away from the π -conjugated framework. In the case of 1-naphthyl derivatives **1k,s** and 1-pyrenyl one **1l**, the cation radicals are also stable since they are also *o*-substituted phenyl derivatives. The values of the oxidation potentials are dependent on the substituents. BEDT-TTF analogues **1o,s** show lower first oxidation potentials than the non-substituted one **1t** and even TTF, indicating that they are stronger electron donors. The differences between the first and second oxidation potentials are smaller than those of TTF and BEDT-TTF, indicating the reduced on-site Coulombic repulsion in **1** due to the extended π -conjugation.

Electrochemical oxidation of **1j** and **1p** gave the cation radical salts **1j**·PF₆ and **1p**·Au(CN)₂ as stable single crystals with stoichiometries of 1:1. These are the first examples of cation radical salts of TTF vinylogues containing substituents at the vinyl positions. In order to investigate the geometries of the donors, X-ray structure analyses of the neutral compounds **1a,j**

Table 1 Oxidation potentials of donors 1^a

Compound	R,R	R ¹	E/V
1a	(CH=CH) ₂	Me	0.71 (2e)
1b	(CH=CH) ₂	Ph	0.61 (2e)
1c	(CH=CH) ₂	<i>o</i> -MeC ₆ H ₄	0.44, 0.62
1d	(CH=CH) ₂	<i>o</i> -ClC ₆ H ₄	0.53, 0.75
1e	(CH=CH) ₂	<i>o</i> -OMeC ₆ H ₄	0.42, 0.63
1f	(CH=CH) ₂	<i>o</i> -NO ₂ C ₆ H ₄	0.59, 0.76
1g	(CH=CH) ₂	<i>p</i> -ClC ₆ H ₄	0.67 (2e)
1h	(CH=CH) ₂	<i>p</i> -OMeC ₆ H ₄	0.58 (2e)
1i	(CH=CH) ₂	<i>m</i> -NO ₂ C ₆ H ₄	0.73 (2e)
1j	(CH=CH) ₂	2,6-F ₂ C ₆ H ₃	0.66, 0.85
1k	(CH=CH) ₂	1-naphthyl	0.47, 0.71
1l	(CH=CH) ₂	1-pyrenyl	0.50, 0.70
1m	SCH ₂ CH ₂ S	Me	0.51 (2e)
1n	SCH ₂ CH ₂ S	Ph	0.49 (2e)
1o	SCH ₂ CH ₂ S	<i>o</i> -MeC ₆ H ₄	0.30, 0.54
1p	SCH ₂ CH ₂ S	<i>o</i> -ClC ₆ H ₄	0.38, 0.60
1q	SCH ₂ CH ₂ S	<i>p</i> -ClC ₆ H ₄	0.52 (2e)
1r	SCH ₂ CH ₂ S	2,6-F ₂ C ₆ H ₃	0.51, 0.70
1s	SCH ₂ CH ₂ S	1-naphthyl	0.33, 0.58
1t	SCH ₂ CH ₂ S	H	0.37, 0.56
1u	H	2,6-F ₂ C ₆ H ₃	0.42, 0.65
TTF			0.35, 0.79
BEDT-TTF			0.50, 0.85

^a 0.1 mol dm⁻³ Bu₄NPF₆ in PhCN, Pt electrode, scan rate 100 mV s⁻¹, E/V vs. SCE.

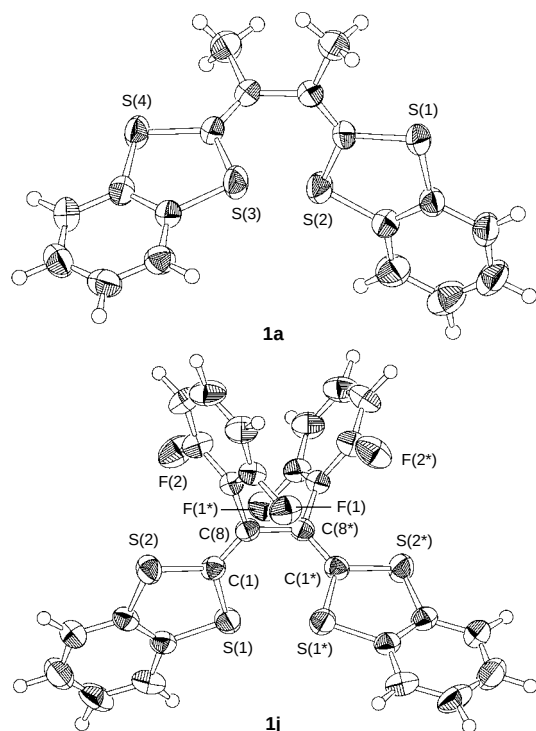


Fig. 1 Molecular structures of **1a** and **1j**

and the cation radical salts **1j**·PF₆ and **1p**·Au(CN)₂ were carried out.† As expected from the CV data, the methyl derivative **1a** has a non-planar structure (Fig. 1) as found in the substituted TTF vinylogues.^{4c,d,e} The *o*-substituted phenyl derivative **1j** which undergoes step-wise oxidation was expected to have a planar TTF vinylogue framework. However, the structure was revealed to be similarly non-planar, as shown in Fig. 1. In contrast, the molecular structure is drastically changed upon oxidation. The cation radical salt **1j**·PF₆ has a planar TTF vinylogue skeleton, as shown in Fig. 2. The aryl groups are twisted and almost orthogonal to the TTF vinylogue framework. The dihedral angle between the aryl group and the 1,3-dithiole ring is 83.9°. The C(1)–C(8) bond length [1.400(8) Å] in the cation radical salt is longer than that of the neutral **1j** [1.354(6) Å], while the C(8)–C(8*) bond length [1.41(1) Å] is shorter than the corresponding one in the neutral species [1.481(8) Å]. This fact suggests the contribution of a delocalized structure **4**. The donor molecules form an interesting two-dimensional columnar structure, as shown in Fig. 2. The bulky aryl groups disturb good overlapping between molecules. Instead, one molecule bridges two others; the 1,3-benzodithiole moieties form a stacking with an equal intermolecular distance of 3.6 Å. The side view of the crystal structure (Fig. 2, bottom) clearly shows a stair-like network where two-dimensional interactions can be expected. The donor molecule in **1p**·Au(CN)₂ also has a planar geometry of its TTF vinylogue framework. The unique crystal structure will be reported elsewhere. Unfortunately, these cation radical salts have a 1:1 stoichiometry and so they showed semiconducting behavior (**1j**·PF₆: $\sigma = 3 \times 10^{-6}$ S cm⁻¹, $E_a = 0.18$ eV; **1p**·Au(CN)₂: $\sigma = 10^{-2}$ S cm⁻¹, $E_a = 0.11$ eV). Studies on the preparation of other cation radical salts of **1** are now in progress.

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Notes and References

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‡ Crystal data for **1a**: C₁₈H₁₄S₄, $M = 358.55$, monoclinic, $P2_1/c$, $a = 12.1233(4)$, $b = 7.4016(3)$, $c = 18.5788(6)$ Å, $\beta = 98.196(3)^\circ$, $V = 1650.08(9)$ Å³, $Z = 4$, $T = 296$ K, $\mu(\text{Cu-K}\alpha) = 52.11$ cm⁻¹, independent

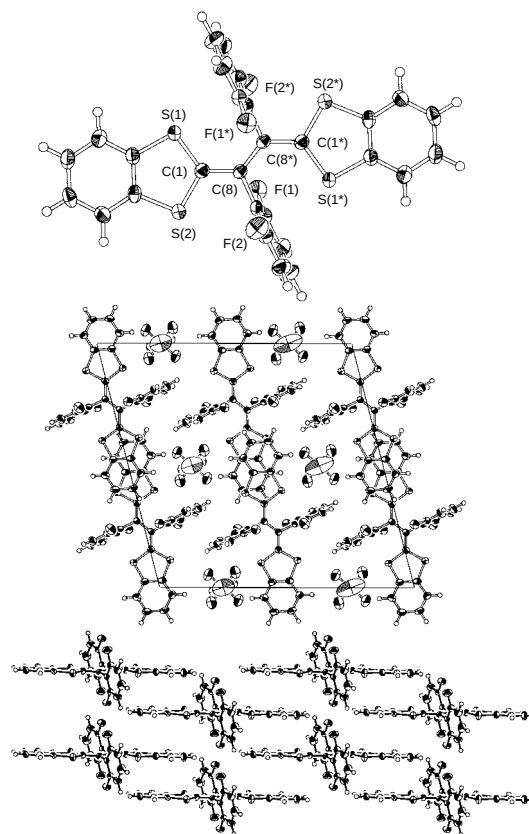


Fig. 2 Crystal structure of **1j**·PF₆. Top: structure of the donor molecule. Middle: projection along the *b*-axis. Bottom: view perpendicular to the stacking axis *b*.

reflections 3640, $R = 0.055$ for 2812 data with $I > 3\sigma(I)$. For **1j**: C₂₈H₁₄F₄S₄, $M = 554.65$, orthorhombic, $Pbcn$, $a = 20.124(9)$, $b = 8.724(7)$, $c = 14.258(5)$ Å, $V = 2503(3)$ Å³, $Z = 4$, $T = 296$ K, $\mu(\text{Mo-K}\alpha) = 4.26$ cm⁻¹, independent reflections 3283, $R = 0.037$ for 1166 data with $I > 3\sigma(I)$. For **1j**·PF₆: C₂₈H₁₄F₁₀PS₄, $M = 699.62$, monoclinic, $C2/c$, $a = 19.814(2)$, $b = 7.1181(6)$, $c = 20.069(1)$ Å, $\beta = 104.588(6)^\circ$, $V = 2739.3(4)$ Å³, $Z = 4$, $T = 296$ K, $\mu(\text{Cu-K}\alpha) = 45.65$ cm⁻¹, independent reflections 3036, $R = 0.058$ for 1303 data with $I > 3\sigma(I)$. For **1p**·Au(CN)₂: C₂₈H₁₆AuCl₂N₂S₈, $M = 880.78$, monoclinic, $P2_1/c$, $a = 10.527(1)$, $b = 11.025(1)$, $c = 13.001(3)$ Å, $\beta = 100.26(2)^\circ$, $V = 1484.8(4)$ Å³, $Z = 2$, $T = 296$ K, $\mu(\text{Cu-K}\alpha) = 164.1$ cm⁻¹, independent reflections 3021, $R = 0.056$ for 2173 data with $I > 2\sigma(I)$. CCDC 182/905

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