The lithium enolate **1** crystallized as a tetramer from benzene, while the enolate **3** crystallized as a dimer from THF.[5] In both **1** and **3** the lithium atoms are tetracoordinate and are coordinated to a single pyrrolidine nitrogen atom. Besides the obvious difference in aggregation state, another significant difference between **1** and **3** is the incorporation of THF into the latter aggregate. It is noteworthy that the presence of the coordinating solvent THF leads to a dimer rather than a tetramer.

Comparison of the crystallographically independent lithium enolate residues in **1** and **3** reveals no significant conformational differences among these species.[6] Thus, a computer generated plot overlaying a single enolate residue from both **1** and **3** is depicted schematically in the Supplementary Material with atom labels inserted. Some average structural parameters for the enolates depicted are given in Table II, also in the Supplementary Material.

For the four crystallographically independent enolate residues in the tetramer **1**, the rms torsion angle corresponding to C(1)-C(2)-C(3)-C(4) is 129.0 (0.6)°; the analogous torsion angle in the dimer **3** is −144.1 (0.5)°. Hence, there is considerable deviation from an anti-periplanar s-trans conformation about the C(2)-C(3) bond in both enolates. In both **1** and **3**, the pyrrolidine nitrogens are pyramidal and are an average of 0.40 Å out of the plane formed by the three covalently attached carbon atoms. This geometry is to be expected since each of the nitrogen atoms are coordinated to a single Li atom.

As typically observed for simple enamines,[7] one of the C-N bonds of each of the pyrrolidine rings is nearly eclipsed with the C-C π-bond. Thus the rms torsion angle for the four crystallographically independent enolates, corresponding to C(4)-C(3)-N(1)-C(7) in structure **9**, is 5.9 (0.9)° for the tetramer **1** and −2.4 (0.4)° for the dimer **3**. Hence there are no strikingly different structural features between **1** and **3** other than the increased steric hindrance in **3** caused by the 2,5-dimethyl substitution on the pyrrolidine rings.

Both enolates, **1** and **3**, have been found to react in a kinetically controlled manner at C-4 to give anti and syn aldol products, respectively, and to so behave with a wide variety of aldehydes. In view of their close structural similarity, the origin of the stereochemical divergency found for these enolates must arise from different reaction transition states. We are currently attempting to delineate these differences.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters along with a computer-generated plot of the dimethylpyrrolidine vinylogous urethane enolate and tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and torsion angles along with a red-green plot of the overlapping major and minor orientations for the pyrrolidine vinylogous urethane enolate (19 pages). Ordering information is given on any current masthead page.

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(5) The pyrrolidine vinylogous urethane enolate **1** crystallized in the centrosymmetric, triclinic space group $P\bar{1}$. The unit cell parameters were determined to be a = 9.902 (4) Å, b = 11.463 (7) Å, c = 19.853 (11) Å, α = 82.49 (5)°, β = 84.37 (4)°, and γ = 75.70 (4)°. This unit cell contained two enolate tetramers of molecular formula $(C_{10}H_{18}NO_2Li)_4$ in a volume of 2159.8 (1.2) Å^3 which produces a calculated density of 1.12 g/cm^3. A total of 5868 reflections were recorded in the range 3.5° $< 2\theta <$ 45°. After accounting for some disorder in the crystal the final agreement factors are R = 0.084 and R_w = 0.095. The dimethylpyrrolidine vinylogous urethane enolate **3** crystallized in the centrosymmetric, monolinic space group $P2_1/n$. The unit cell parameters were determined to be a = 11.712 (3) Å, b = 10.192 (2) Å, c = 14.380 (6) Å, and β = 98.92 (4)°. This unit cell contained two THF-solvated enolate dimers of molecular formula $[(C_{10}H_{18}NO_2Li)\cdot(C_4H_8O)]_2$ in a volume of 1695.8 (1.2) Å^3 which produces a calculated density of 1.12 g/cm^3. A total of 1949 reflections were recorded in the range 3.5° $< 2\theta <$ 45°. The final agreement factors are R = 0.058 and R_w = 0.060.

(6) A computer-generated plot overlaying a single enolate residue from both **1** and **3** is depicted schematically in the Supplementary Material with atom labels inserted. Some average structural parameters for the enolates depicted are given in Table II of the Supplementary Material.

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Synthesis of Bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene, an Annelated TTF Derivative with Good Electron Donor Properties

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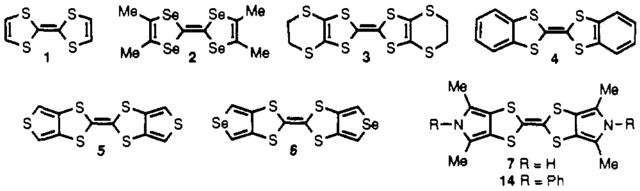
Highly conducting lower dimensional organic metals based on the potent one-electron donor TTF (tetrathiafulvalene, **1**) have been studied intensely in the last 15 years.[1] The salts of TMTSF (tetramethyltetraselenafulvalene, **2**) superconduct below about 1 K,[2] while one salt of ET (bis(ethylenedithiolene)TTF, **3**), namely $ET_2Cu(SCN)_2$, superconducts below T_c = 10.4 K.[3] Several annelated derivatives of TTF (DBTTF = **4**, DTTTF = **5**, DSTTF = **6**) have also been studied in the search for other good one-electron donors,[4-7] but they had considerably higher solution oxidation potentials than TTF.



For binary complexes of a one-electron donor D and a one-electron acceptor A, a good rule of thumb is[8,9] that if the difference $I_D - A_A$ (I_D = ionization potential of D, A_A = electron affinity of A) is too large, then mixed-stack Mulliken π-π charge-transfer complexes with low degree of charge transfer (π-π mixed stacking $D^0A^0D^0A^0$:electrical insulators) are obtained; if $I_D - A_A$ is small, then ionic salts with high charge transfer result (π-π mixed stacking $D^+A^-D^+A^-$: semiconductors); for intermediate $I_D - A_A$ the desired segregated stacking of TTF TCNQ can be achieved ($D^+D^0D^+/A^-A^0A^-$). For ion-radical salts such as $TMTSF_2X$ or ET_2X (X = inorganic anion) no such rule of thumb has emerged.

While annelated TTF derivatives prepared so far (**3-6**) tend to be weaker electron donors than TTF, we report here the synthesis of BP-TTF (bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene, **7**) a pyrrolo-annelated TTF which is a stronger donor than TTF. As shown in Scheme I, the known[10,11] 3,4-dithiocyanatopyrrole (**9**) was prepared in 82% yield (mp 130-2 °C; lit. 134-6

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(1) For a recent review cf.: "Proceedings of International Conference on Synthetic Metals ICSM'86" In *Synthetic Metals*; Shirakawa, H., Yamabe, T., Eds.; Kyoto, Japan, 1987; Vols. 17-19.

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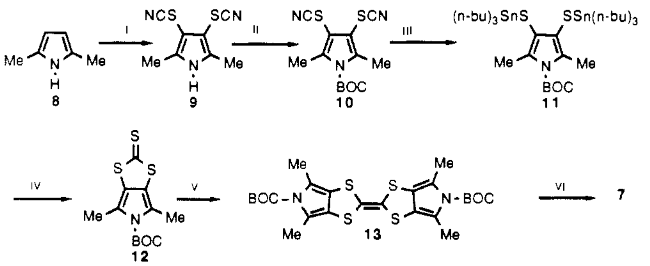
Scheme I



^{a}(i) KSCN, Br_2, MeOH; (ii) $(BOC)_2O$, DMAP, NEt_3; (iii) 2 equiv of tributyltin hydride, C_6H_6; (iv) thiophosgene, C_6H_6; (v) hexabutylditin, C_6H_6, $h\nu$; (vi) 25% NaOMe.

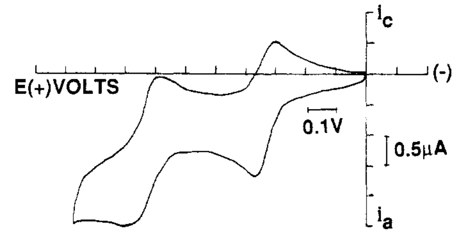


Figure 1. Cyclic voltammogram of 1.0×10^{-4} M BP-TTF, **7**, in CH_3CN, using 0.1 M TBAHFP supporting electrolyte, Pt disk (working) and Pt wire (auxiliary) electrodes, versus an SCE reference electrode. Scan rate 0.050 V/s.

°C); when reacted with di-*tert*-butyldicarbonate [$(BOC)_2O$] it afforded the N-protected pyrrole **10** in 90% yield. Treatment of **10** with 2 equiv of tributyltin hydride[12] yielded **11** (60%). Compound **12**[13] was prepared in 35% yield by adding thiophosgene to a dilute benzene solution of **11**. The coupling reaction of **12**[14] was carried out by the photolysis method of Ueno[15] to give 15–20% of the product **13**. The *N*-*tert*-butoxycarbonyl substituent was removed rapidly under basic conditions to give the final product **7** nearly quantitatively.[16]

Figure 1 gives the cyclic voltammogram of **7**. We report in Table I measured solution oxidation potentials and relevant computed gas-phase ionization potentials. The computed ionization potential of BP-TTF is lower than that of TTF; this result is confirmed by lower solution oxidation potentials. It is clear that BP-TTF is an even better donor than TTF, illustrating the dramatic effect of the annelation by a highly electron-rich pyrrole ring. It should also be noted that facile chemical substitutions at the pyrrole N atoms make this donor particularly versatile. For example, we have already obtained the *N*-phenyl analogue **14** [bis(2,5-dimethyl-1-phenylpyrrolo-[3,4,*d*])tetrathiafulvalene][21] and find (Table I) that this donor has oxidation potentials (and calculated first ionization potential) very similar to those of **7**.

Table I. Half-Wave Solution Oxidation Potentials $E_{1/2}$ (Volts versus SCE),[a] Computed MNDO Vertical Ionization Potentials[b] I_{MNDO} (eV), and Experimental Gas-Phase Ionization Energy[c] I_{exp} (eV)

compd	first $E_{1/2}$	second $E_{1/2}$	I_{MNDO}	I_{exp}
BP-TTF, **7**	0.31	0.70	7.51	
BPP-TTF, **14**	0.39	0.74	7.46	
TTF, **1**	0.35	0.75	8.08	6.85[c]
ET, **3**	0.54	0.96	8.08	
DBTTF, **4**	0.78[d]	1.17[d]	8.02	
DTTTF, **5**	0.75[e]		8.20	

[a] Reference 17. [b] Reference 18. [c] Reference 19. [d] Reference 4. [e] References 5 and 20.

Further studies to improve the yield, widen the scope of applicability, and grow ion-radical salts and charge-transfer complexes of **7** are in progress.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-86-07458) for partial support of this work. We are also indebted to the Office of Naval Research (Grant N-00014-86-G-0215) for the purchase of the MicroVAX-II and to the Alabama Supercomputer Authority for computer time on the Cray X/MP-24.

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[13] Mp 165 °C; *m/e* (rel intensity) 301 (M^+, 32), 245 (31), 201 (13), 57 (100); ^1H NMR δ ($CDCl_3$) 2.37 (6 H, s), 1.60 (9 H, s).

[14] Mp >280 °C; *m/e* (rel intensity) 538 (M^+, 14), 438 (39), 426 (93), 382 (76), 338 (100), 57 (41); ^1H NMR δ ($CDCl_3$) 2.35 (12 H, S), 1.58 (18 H, s).

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[16] Mp >300 °C; *m/e* (rel intensity) 338 (M^+, 100), 213 (53), 169 (14); ^1H NMR δ ($CDCl_3$) 2.17 (s).

[17] $E_{1/2}$ values are obtained as $E_{1/2}$ = oxidation peak −0.030 V in cyclic voltammograms measured in CH_3CN solution (with 0.1 molar TBAHFP supporting electrolyte) with a BAS CV-27 cyclic voltammograph, platinum disk (working), platinum wire (auxiliary), and SCE (reference) electrodes. All waves are reversible.

[18] The MNDO vertical ionization potentials were obtained by using computer program MOPAC version 3.11 on a MicroVAX-II computer or computer program MOPAC 4.01 on a Cray X/MP-24 computer, with geometry optimization of each structure.

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[20] Assuming that V versus SCE = 0.320 + volts versus [Ag]0.1 M $AgNO_3$|0.1 M $LiClO_4$], cf.: Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta* **1961**, *25*, 371.

[21] Compound **14** was synthesized from *N*-phenyl-2,5-dimethylpyrrole by the procedure described in Scheme I.

Monomeric Metaphosphate Formation during Radical-Based Dephosphorylation

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Radical-based dephosphorylation[1,2] via a phosphonyl radical **1a** (Scheme I) constitutes one formulation for the mechanism of carbon-to-phosphorus bond cleavage during microbial degradation of organophosphonates.[3] Chemical precedent for the biotic dephosphorylation follows from chemical and electrochemical oxidation of alkylphosphonic acids.[1a,b] Oxidative approaches have been restricted to analysis of the carbon fragments formed during C–P bond cleavage and provide little information relevant to reactive phosphorus-containing intermediate **2a**. This report describes a nonoxidative method for phosphonyl radical generation which has led to the first evidence for monomeric metaphosphate **2** formation[4,5,9] during radical-based dephosphorylation of orga-

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