Pergamon

Tetrahedron Letters 42 (2001) 1571–1573

TETRAHEDRON
LETTERS

Synthesis of 2,3-dimethylthio-6-pyridyl tetrathiafulvalene: a precursor for a new system involving a direct linkage between a strong donor (D) and a strong acceptor (A)

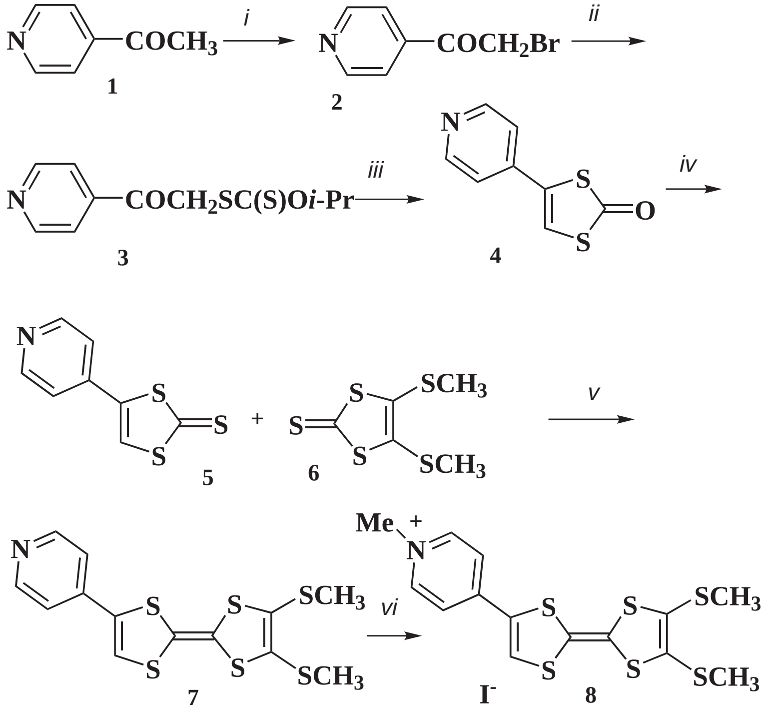
Ofra Paz-Tal Levi, James Y. Becker,* Arkady Ellern and Vladimir Khodorkovsky*

Department of Chemistry, Ben Gurion University of the Negev, Beer Sheva 84105, Israel

Received 6 December 2000; accepted 11 December 2000

Abstract—A multi-step synthesis of a novel tetrathiafulvalene derivative involving a 4-pyridyl substituent directly attached to the TTF moiety is described. © 2001 Published by Elsevier Science Ltd.

There is a growing interest in the preparation of 'D-spacer-A' diads (D-π electron donor; A-π electron acceptor) and study of their intramolecular charge transfer (ICT), electron transfer (ET) and optical properties. The most commonly studied diads involve tetrathiafulvalene (TTF)-based derivatives as the strong electron donor moieties and various electron acceptor moieties, covalently linked via different sigma spacers.[1] Apparently, linking together a very strong donor to a very strong acceptor moiety presents difficult synthetic



Scheme 1. Reagents: (i) Br_2, 40% HBr, 2 h; (ii) NaSC(S)O*i*-Pr, H_2O, 45% overall yield from **1**; (iii) H_2SO_4, 50°C, 1 h, 70%; (iv) P_4S_{10}, *o*-$C_6H_4Cl_2$, 6 h, 65–70%; (v) neat $P(OEt)_3$, 1 h, 15%; (vi) MeI, MeCN, rt, overnight, 96%.

---

* Corresponding author.

0040-4039/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0040-4039(00)02269-3

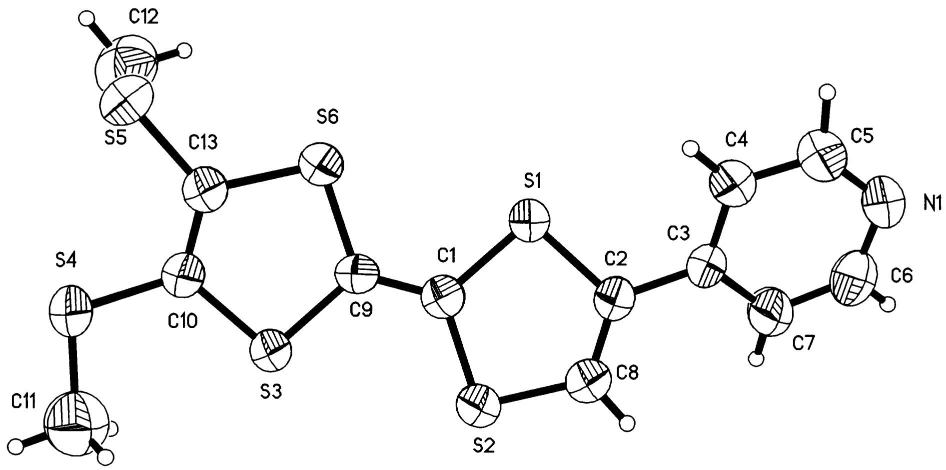


Figure 1. ORTEP drawing of **7** at the 50% probability level. C1–C9 1.332(7), C2–C3 1.468(7), C2–C8 1.322(8), S2–C8 1.705(6), S3–C10 1.747(5), C10–C13 1.337(8) Å. The torsion angle between the pyridine and the dithiole rings is 25.9°.

problems owing to undesired donor–acceptor interactions either at stages preceding the chemical linking or during isolation of the final product.[2]

One of the strongest acceptors used for linking with the TTF moiety, by a unique approach, is the *N*-alkyl pyridinium cation in a TTF-sigma spacer-Py^+ system.[3] Derivatives involving both TTF and Py^+ moieties are excellent models for studying ICT versus ET processes since the formation of the strong accepting moiety occurs on the very last stage of the synthesis, and under mild and controllable conditions.

Recently a TTF-π-spacer-Py^+ system with an ethenyl π spacer was prepared.[4] In the present communication we report a simple synthetic route for the synthesis of a D–A system in which the TTF moiety is directly linked to the pyridinium cation moiety, without any spacer, according to Scheme 1. Attempts to apply the known procedure described for the synthesis of aryl substituted 1,3-dithiole-2-thiones from the corresponding 1,3-dithiole-2-(*N*-diethyl)immonium salt[5] for the key precursor, 4-(4′-pyridyl)-1,3-dithiole-2-thione **5**, have been unsuccessful. However, the cyclization of **3** in concentrated sulfuric acid afforded 1,3-dithiole-2-one derivative **4** in 70% yield. Derivative **5** can be obtained in 65–70% yields upon treatment with phosphorus sulfide. Although the coupling between **5** and 4,5-dimethylthio-1,3-dithiole-2-thione[6] with triethyl phosphite gives the unsymmetrical TTF derivative **7** in low yields along with symmetrical derivatives, chromatographic separation is simple due to the large difference in R_f of the products. Long chain substituted alkylthio substituted derivatives can also be easily prepared according to the above protocol (for instance, the 2,3-dihexadecylthio derivative of **7** in 12% yield).

Cyclic voltammetry of derivative **7** in acetonitrile exhibits two reversible oxidation waves, $E_{1/2}(1) = 0.49$ V and $E_{1/2}(2) = 0.76$ V (versus Ag/AgCl), almost identical to the values obtained for dimethylthio-TTF ($E_{1/2}(1) = 0.45$ V; $E_{1/2}(2) = 0.76$ V). The structures of derivatives **3**, **4** and **7** were determined by X-ray diffraction measurements[7] of single crystals. The crystal structure of **7** (Fig. 1) shows no intermolecular interactions, although the stack is segregated along a diagonal axis. The interplanar distances between the planes of pyridine–pyridine and TTF–TTF are longer than 5.7 Å.

Alkylation of **7** is facile using 3–4-fold excess of methyl iodide at room temperature in acetonitrile or acetone, from which product **8** precipitates as black crystals. Salt **8** exhibits an ICT absorption band at $\lambda_{max} = 572$ nm in ethanol, which does not correspond to any of the TTF or pyridinium moieties, and obeys the Beer–Lambert law. The position of this band is solvent dependent: a blue shift in DMSO solutions (540 nm) and a red shift in methylene chloride (618 nm) were observed. Two reversible oxidation waves were observed for this compound at higher potentials ($E_{1/2}(1) = 0.58$ V and $E_{1/2}(2) = 0.81$ V (versus Ag/AgCl)) in agreement with the electron accepting nature of the substituent. Photochemical properties of **8** are similar to the analog involving the trimethyl TTF donor unit[8] and will be discussed in detail elsewhere.

Acknowledgements

This work was partially supported by a grant from the Ministry of Science, Israel.

References

1. (a) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11; (b) Tsiperman, E.; Regev, T.; Becker, J. Y.; Bernstein, J.; Ellern, A.; Khodorkovsky, V.; Shames, A.; Shapiro, L. *J. Chem. Soc., Chem. Commun.* **1999**, 1125.
2. (a) Bryce, M. R. *Adv. Mater.* **2000**, *10*, 589; (b) Panetta, C. A.; Baghdadchi, J.; Metzger, R. M. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 103.

3. (a) Goldenberg, L. M.; Becker, J. Y.; Paz-Tal Levi, O.; Khodorkovsky, V.; Bryce, M. R.; Petty, M. C. *J. Chem. Soc., Chem. Commun.* **1995**, 475; (b) Goldenberg, L. M.; Becker, J. Y.; Paz-Tal Levi, O.; Khodorkovsky, V.; Shapiro, L. M.; Bryce, M. R.; Cresswell, J. P.; Petty, M. C. *J. Mater. Chem.* **1997**, *7*, 901.
4. Andreu, R.; Malfant, I.; Lacroix, P. G.; Cassoux, P. *Eur. J. Org. Chem.* **2000**, 737.
5. Fanghänel, E. *Z. Chem.* **1967**, *1*, 58.
6. Hartke, K.; Kissel, T.; Quante, J.; Matusch, R. *Chem. Ber.* **1980**, *113*, 1898.
7. Intensity data for X-ray structure determination of **4** were collected using a Bruker diffractometer (6K CCD detector, λ(Mo Kα) = 0.711069 Å, graphite monochromator, 1080 frames with a scan width of 0.3° in ω for hemisphere coverage of reciprocal space and 50 frames for decay correction, exposure time of 10 s/frame, detector–crystal distance 4.95 cm, integration with Bruker SAINT software package using a wide-frame integration algorithm. Data were corrected for absorption using SADABS program) and Syntex P-1 conventional diffractometer for **3** and **7** (λ(Mo Kα) = 0.711069 Å, graphite monochromator, $2\theta/\omega$-scan). All structures were solved by direct methods and refined by least-squares in full-matrix anisotropic approximation for all nonhydrogen atoms. The hydrogen atoms were included with geometrically calculated positions and refined using a 'riding model'. Bruker SHELX software package was used for all calculations and drawings. Atomic coordinates, bond lengths and angles, and anisotropic parameters have been deposited at the Cambridge Crystallographic Data Center. **7**: an orange plate (0.4×0.4×0.1 mm) is monoclinic, $C_{13}H_{11}NS_6$, space group $P2_1/c$, at 293 K, $a = 13.601(4)$, $b = 13.197(3)$, $c = 9.289(2)$ Å. $\beta = 106.54(3)°$, $V = 1598.3(7)$ Å^3, $Z = 4$, $F(000) = 768$. 2205 reflections were collected ($2\theta < 45.2°$), of which 2106 reflections were independent ($R_{int} = 0.0380$). Structure was refined to $R_1 = 0.0570$, $wR_2 = 0.1621$, GOF = 1.042, 196 parameters.
8. Moore, A. J.; Batsanov, A. S.; Bryce, M. R.; Howard, J. A. K.; Khodorkovsky, V.; Shapiro, L.; Shames, A. *Eur. J. Org. Chem.* **2001**, *73*.