Protonation of Oligothiophenes

Yuan Yu, Esmir Gunic, and Larry L. Miller*

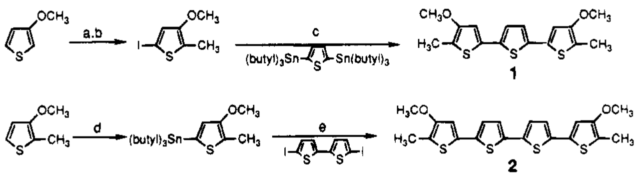
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Received December 13, 1994

Oligothiophenes have received attention as models for conducting polymers and as compounds with intrinsically interesting optical and electrical properties.[1-7] Of particular interest to us and others has been the oxidation of these compounds to form cation radicals and dications, species that are models for polarons and bipolarons[8] in oxidized, conducting polythiophene. A particular discovery from this work is that cation radicals form π-dimers in dilute solution[2] and in solid films.[6,7] These diamagnetic interchain dicationic dimers are alternatives to intrachain bipolarons (dications). Here we describe diamagnetic oligothiophene monocations. Definition of the spectral qualities of such cations should allow them to be detected (or ruled out) in various reactions involving oligo- and polythiophenes.

We report on cations formed by protonation of the terminally blocked, methoxy-substituted oligothiophenes **1** and **2**. These oligomers were chosen with the hope that various cations derived from them would be stable. The synthetic approach[2,3] is described in Scheme 1. Products **1** and **2** were characterized by ^1H NMR (Table 1), ^{13}C NMR, HR-MS, IR, and UV−vis (Table 1). Spectral comparisons with other oligomers were satisfactory. For example, the terthiophene **3**[2b] (λ_{max} = 360 nm) and the quatrathiophene **4**[3] (λ_{max} = 396 nm) can be compared with **1** (λ_{max} = 386 nm) and **2** (λ_{max} = 414 nm).

Scheme 1[a]

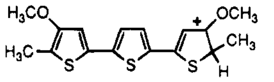


[a] n−Butyllithium, dimethyl sulfate (80%). [b] n-Butyllithium, I_2 (75%). [c] Toluene, $[(C_6H_5)_3P]_4Pd$ (30%). [d] n-Butyllithium, $(butyl)_3SnCl$ (85%). [e] Toluene, $[(C_6H_5)_3P]_4Pd$ (35%).

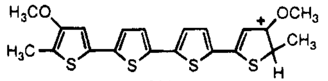
Table 1. Spectral Data[a]

compound	λ_{max} (nm)	NMR δ (ppm) (J (Hz))
1	386	6.95 (1H, s), 6.86 (1H, s), 3.85 (3H, s), 2.27 (3H, s)
1H$^+$	590	8.08 (1H, d, 4.6 Hz), 7.43 (1H, d, 4.6 Hz), 7.34 (1H, s) 6.80 (1H, s), 4.84 (1H, q, 7.4 Hz), 4.26 (3H, s) 3.93 (3H, s), 2.39 (3H, s), 1.82 (3H, d, 7.4 Hz)
2	414	7.02 (1H, d, 3.8 Hz), 6.97 (1H, d, 3.8 Hz), 6.87 (1H, s) 3.84 (3H, s), 2.27 (3H, s)
2H$^+$	630	8.11 (1H, d, 4.2 Hz), 7.65 (1H, d, 3.9 Hz), 7.55 (1H, d, 4.2 Hz), 7.27 (1H, d, 3.9 Hz), 7.16 (1H, s) 6.72 (1H, s), 4.91 (1H, q, 7.5 Hz), 4.30 (3H, s) 3.96 (3H, s), 2.35 (3H, s), 1.84 (3H, d, 7.5 Hz)

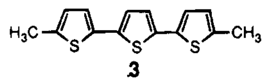
[a] NMR spectra at 300 MHz.



1H$^+$



2H$^+$



3

The yellow compound **1** treated with 5% trifluoroacetic acid (TFA) in CD_2Cl_2 instantly gave a deep blue, ESR silent solution with the ^1H NMR spectra described in Table 1. In the range 200−2600 nm there was one optical absorption peak at 590 nm. These spectra were stable for days and were formed identically in deoxygenated solution. Both vis and NMR spectra are consistent with formation of cation **1H**$^+$. Notable in comparison to the NMR spectrum of **1** is the shift of the **1H**$^+$ resonances to higher δ values (delocalized positive charge), a separate resonance for each type of hydrogen (loss of symmetry) and one additional hydrogen appearing as a quartet at δ 4.85 (coupled to the adjacent teminal methyl group with J = 7.4 Hz). The structure was confirmed by using TFA-d_1 to form **1D**$^+$, which showed two spectral changes compared to **1H**$^+$: no peak at 4.85 and a broadened singlet (unresolved 1.1 Hz J_{H-D}), not a doublet, for the terminal methyl group.

Compound **2** behaved analogously (Table 1) giving **2H**$^+$. Addition of water to the solutions immediately regenerated **1** and **2**.

Although a number of solid conducting polymers have been formed by protonation[8,9] and oligothiophenes have been oxidized in TFA[2c] this is the first documentation of oligothiophene protonation. The methoxy groups enhance the basicity of these oligomers (**3H**$^+$ is not formed from **3** in 80% TFA, 20% CH_2Cl_2), but the spectra clearly demonstrate that **1H**$^+$ and **2H**$^+$ are delocalized ions. Therefore, the spectral results are relevant to understanding other oligothiophene, polythiophene, and related oligo(thienylenevinylene) chemistry. Of general interest is the observation that authentic dications (bipolarons) and monocations from similar oligomers absorb at very similar wavelengths in the visible region, e.g., **1H**$^+$ 590 nm and **3**$^{2+}$ 570 nm.[2b]

---

(1) See 2−7 and references therein.

(2) (a) Chang, A. C.; Miller, L. L. *Synth. Met.* **1987**, *22*, 71. (b) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F.; Zinger, B. *Chem. Mater.* **1992**, *4*, 1106. (c) Zinger, B.; Mann, K. R.; Hill, M. G.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1113.

(3) Tour, J. M.; Wu, R. L. *Macromolecules* **1992**, *25*, 1901. Guay, J.; Kasai, P.; Diaz, A.; Wu, R. L.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.

(4) Bauerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217. Bauerle, P.; Segelbacher, U.; Gaudl, K. U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.

(5) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, *39*, 243. Fichou, D.; Horowitz, G. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 379.

(6) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater*, **1993**, *5*, 430. Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620. Zotti, G.; Berlin, A.; Pagani, G.; Schiavon, G.; Zecchin, S. *Adv. Mater.* **1994**, *6*, 231.

(7) Hotta, S.; Waragai, K. *J. Phys. Chem.* **1993**, *29*, 7427.

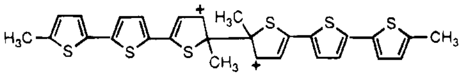
(8) Han, C. C.; Elsenbaumer, R. L. *Synth. Met.* **1989**, *30*, 123.

(9) Huang, W. S.; MacDiarmid, A. G.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1784.

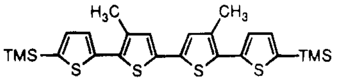
0897-4756/95/2807-0255$09.00/0

This will make them difficult to differentiate. Of specific interest is a report based on visible absorption spectra that oligo(thienylenevinylene)s like **5** are protonated twice in neat TFA to produce dications.[10] Since these oligomers are extremely similar to oligothiophenes (**5** has 10 double bonds, **2** has 8) the spectral similarities of mono- and dications should be valid. We suggest that monocations from monoprotonations should now be considered as reasonable alternative structures.

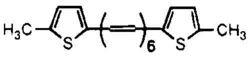
With regard to oxidized oligothiophenes the data in Table 1 can be used to differentiate σ- and π-dimers[2,4,6,7] of cation radicals. Consider the dimer of cation radical **3**$^{+\cdot}$.[2b] It has NIR absorption bands and has been proposed to be a π-dimer. The alternative σ-dimer is σ-(**3**$^+$)$_2$. Since each of the two π-systems of σ-(**3**$^+$)$_2$ are similar to **1H**$^+$ and electronically insulated from each other by two sp^3 carbons, the σ-dimer should absorb in the visible, not the NIR as observed experimentally.



σ-(**3**$^+$)$_2$



4



5

Our future work will explore several of these questions and further define the basicity of oligothiophenes.

Acknowledgment. Interest in protonation was stimulated by Baruch Zinger. Financial support was provided by NSF.

CM940551M

---

[10] Spangler, C. W.; Bryson, P.; Liu, P. K.; Dalton, L. R. *J. Chem. Soc., Chem. Commun.* **1992**, *2*, 253.