ORGANIC LETTERS

2001
Vol. 3, No. 11
1673−1675

A Simple Route to *N*-Arylated 2-Aminothiophenes as a New Class of Amorphous Glass Forming Molecules

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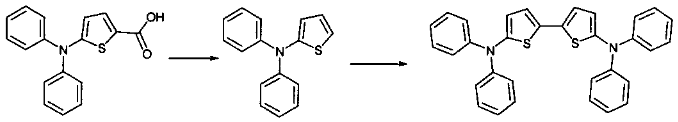
Received March 22, 2001

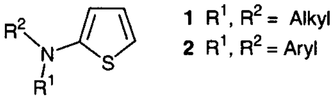
ABSTRACT



By thermal decarboxylation of *N*-arylated 2-aminothiophene-5-cacrboxylates, a versatile, heavy-metal free method for preparing the title compounds as new class of highly reactive and easily oxidable, amorphous glass forming molecules has been elaborated.

As pointed out recently,[1] 2-dialkylaminothiophenes **1** (Scheme 1) are among the most interesting developments in dye chemistry of the past few years. When these compounds are substituted with strong electron acceptors at the 5-position, they exhibit enhanced nonlinear optical (NLO) properties which significantly exceed those of the corresponding dialkylaniline derivatives.[2] Moreover, 5-(dimethylamino)-5′-nitro-2,2′-bithiophene is among the best indicators for studying the solvent polarity due to its outstanding positive solvatochromism.[3]

Scheme 1



Despite these advantages, the mentioned 2-(dialkylamino)-thiophene derivatives have a disadvantage. They exhibit a relatively low thermal stability, which restricts, e.g., their use in NLO applications. Here a pooling procedure at elevated temperatures is an essential precondition for their practical use in this field.[4] As exemplified with some NLO-active azo or methine dyes, the thermal stability of *N*,*N*-disubstituted 2-aminothiophene compounds can be significantly increased if their amino moiety is aryl-substituted.[5] Therefore, *N*,*N*-diaryl-substituted 2-aminothiophenes **2** gained prominence as building blocks for preparing the above-mentioned dyes. Moreover, such compounds received, as exemplified by a few authors recently,[6,7] some attention as building blocks for new materials, exhibiting a high tendency to form stable radical cations and a high tendency to form amorphous glasses in which the radical cations formed by oxidation possess a strong mobility. These materials can be used for constructing special optical and/or electronic devices, such as organic luminescence diodes[8] or organic field-effect transistors.[9]

Currently, *N*,*N*-diaryl-substituted 2-aminothiophenes **2** are, in contrast to their *N*,*N*-dialkyl-substituted analogues **1**, nearly

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[1] Wuerthner, F.; Thalacker, C.; Matschiner, R.; Kukaszuk, K.; Wortmann, R, *Chem. Commun*. **1998**, 1739.

[2] Wolff, J. J.; Wortmann, R. *Adv. Phys. Org. Chem*. **1999**, *32*, 121. Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *Chem. Commun*. **1990**, 90.

[3] Effenberger, F.; Wuerthner, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 719.

[4] Bosshard, C.; Sutter, K.; Pretre, P.; Hulliger, J.; Floersheimer, M.; Kaatz, P.; Guenther, P. *Organic Nonlinear Optical Materials*; Gordon and Braech: Basel, 1995.

[5] Jen, A. K.-Y.; Cai, Y.; Bedworth, P. V.; Marder, S. R. *Adv. Mater*. **1997**, *9*, 132. Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Miller, R. D.; Volksen, W.; Thackare, J. I. And Walsh, C. A. *SPIE* **1994**, *2285*, 17. Twieg, R. J.; Burland, D. M.; Hedrick, J.; Lee, V. Y.; Miller, R. D.; Moylan, C. R.; Seymour, C. M.; Volksen, W.; Walsh, C. A. *SPIE* **1994**, *2143*, 2.

[6] Ueta, E.; Nakano, H.; Shirota, Y. *Chem. Lett.* **1994**, 2397.

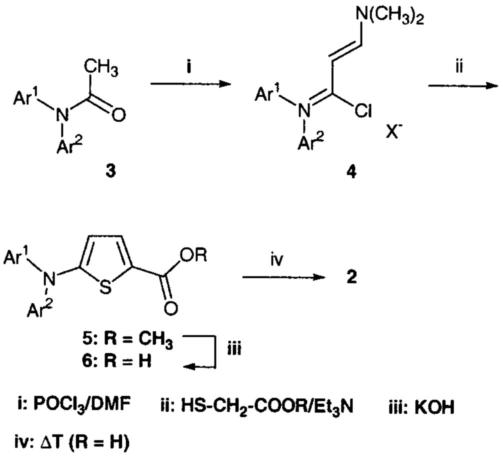
[7] Wu, I.-Y.; Lin, J. T.; Tao, Y.-T.; Balasubramaniam, E. *Adv. Mater*. **2000**, *12*, 668.

10.1021/ol015875c CCC: $20.00

unknown. The few known derivatives of this series have been prepared by a heavy-metal catalyzed C−N coupling reaction starting from diarylamines and 2-halothiophenes. For instance, 2-diphenylaminothiophene **2a** has been prepared either by a copper-mediated Ullmann reaction[10] or in the course of a palladium-catalyzed coupling reaction[11] from 2-bromothiophene and diphenylamine. Satisfactory yields of products could only be obtained, however, by using special reaction conditions. Thus, in the copper-catalyzed reaction, stoichiometric amounts of copper iodide and a polar aprotic solvent, such as HMPT, were necessary, and in the palladium-catalyzed reaction special phosphine ligands for activating the palladium catalyst were necessary. The desired products thereby obtained are usually contaminated with heavy-metal impurities. Their separation is urgently necessary for the practical use of the products, e.g, as electronic material, resulting in a time- and cost-consuming procedure which raises the price of such products significantly.

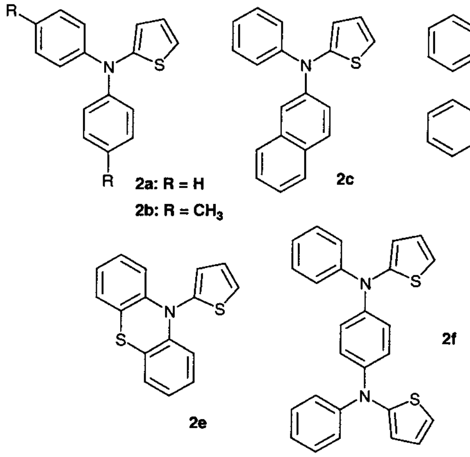
To overcome these difficulties, a simple synthesis of *N*-arylated 2-aminothiophenes **2** has been elaborated. This method follows a known route for preparing *N*-disubstituted 2-aminothiophenes[12] and starts from *N*-acetylated diarylamines **3** which were transformed, at first, by means of a Vilsmeier−Haak−Arnold reaction via the 1-chlorovinamidinium salts **4**[13] into the *N*-diaryl derivatives of alkyl 2-aminothiophene-5-carboxylates **5**.[14] Subsequently, these alkyl thiophene carboxylates **5** were transformed by reaction with aqueous bases into the corresponding free acids **6** from which the carboxy group free thiophenes **2** can be obtained by thermal decarboxylation (Scheme 2).

Scheme 2



The decarboxylation can be performed either by heating the 2-aminothiophene-5-carboxylic acids **6** at their decomposition temperature or by refluxing the acids **6** in acetic acid until the evolution of carbon dioxide ceases. Thus, by these methods the *N*-diarylated 2-aminothiophene derivatives **2a**−**2f** have been prepared in yields between 44 and 92% (Scheme 3). Their structures as well as the structures of their precursors **3**−**6** were confirmed by analytical and spectroscopic data.

Scheme 3



As expected, the *N*-arylated 2-aminothiophenes **2a**−**2f** exhibit low oxidation potentials. Also, in contrast to their *N*-alkylated derivatives, e.g., the 2-morpholino derivative **2g**, they exhibit a strong tendency to form, after cooling their melts, stable amorphous glasses. Their T_gs could by measured by DSC under nitrogen and with a heating rate of 5 K min^{-1} (see Table 1). This method, which was very recently applied to the estimation of T_gs of certain dyes derived from *N*,*N*-disubstitued 2-aminothiophens,[15] was also useful for estimating the melting points (T_m[A]) of the 2-aminothiophene-5-

Table 1. Thermal and Electrochemical Data of the *N*-Diarylated 2-Aminothiophenes **2** and Their Precursors **6**

entry	T_m[A] [°C]	entry	T_m[H] [°C]	T_g[H] [°C]	T_d[H] [°C]	E_{ox}[a] [V]
6a	157	**2a**	83	−29	274	+0.86
6b	166	**2b**	62	−23	303	+0.82
6c	167	**2c**	102	±0	272	+0.87
6d	155	**2d**	104	+2	332	+0.92
6e	181	**2e**	109	−21	345	+1.17
6f	163	**2f**	83	−8	358	+0.65[b]
6g[c]	157	**2g**[d]	20		305	+0.55

[a] Measured toward the SCE, irreversible potentials. [b] Reversible potential. [c] 2-Morpholinothiophene-5-carboxylic acid.[12] [d] 2-Morpholinothiophene.

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(8) Rothberg, L. J.; Lovinger, A. J. *J. Mater. Res.* **1996**, *11*, 3174.

(9) Brown, A. R.; Jarrett, C. P., deLeeuw, D. M.; Matters, M. *Synth. Methods* **1997**, *88*, 37.

(10) Bedworth, P. V.; Cai, K.-Y.; Jen, A.; Marder, S. R. *J. Org. Chem.* **1996**, *61*, 2242.

(11) Watanabe, M.; Yamamoto, T.; Nishiyama, M. *Chem. Commun.* **2000**, 133.

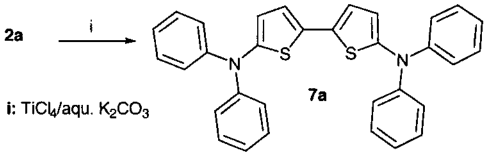
(12) Liebscher, J.; Hartmann, H. *J. Prakt. Chem.* **1971**, *318*, 731. Liebscher, J.; Hartmann, H. *Synthesis* **1979**, 241. Liebscher, J.; Abegaz, B.; Areda, A. *J. Prakt. Chem.* **1983**, *325*, 168. Liebscher, J.; Feist, K. *Synthesis*, **1985**, 412. Hartmann, H.; Eckert, K.; Schröder, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 556.

carboxylates **6** as well as the melting points (T_m[H]) and the decomposition points (T_d[H]) of the resulting 5*H*-substituted *N*-arylated 2-aminothiophenes **2**.

To verify that the observed T_gs are really glass transition temperatures and do not originate from other relaxation processes, the corresponding transition energies were estimated. They are generally in the range of 0.2−0.3 J g^{-1} K^{-1}. Furthermore, the measurements were repeated a second and a third time. No significant changes were observed in course of these runs.

Owing to the free 5-position at the 2-aminothiophene moieties, the electrochemical oxidation of the compounds **2a**−**2f** was found to be irreversible, indicating that in course of this process an oxidative dimerization occurs. For compound **2a**, the resulting dimer **7a** was alternatively synthesized by a controlled chemical oxidation using $TiCl_4$ as reagent, according to the recently published method of M. Periasamy et al.[16] (Scheme 4).

Scheme 4



Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: Experimental procedures and full charaterization for compounds **2a**−**2f** (^{1}H NMR spectral data). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Arnold, Z. *Collect. Czech. Chem. Commun*. **1961**, *26*, 3051. Schroth, W.; Jahn, U.; Ströhl, D. *Chem. Ber*. **1994**, *127*, 2013.

(14) Hartmann, H.; Heyde, C.; Zug, I. *Eur. J. Org. Chem*. **2000**, 3273.

(15) Wuerthner, F.; Yao, S.; Schilling, J.; Wortmann, R.; Redi-Abshiro, M.; Mecher, E.; Gallengo-Gomez, F.; Meerholz, K. *J. Am. Chem. Soc*. **2001**, *123*, 2810.

(16) Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem*. **2000**, *65*, 3548.