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

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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



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 NLOactive 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 abovementioned 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 diodes⁸ or organic field-effect transistors.⁹

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

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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 reaction¹⁰ or in the course of a palladium-catalyzed coupling reaction¹¹ 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-aminothiophenes¹² and starts from *N*-acetylated diaryl-amines **3** which were transformed, at first, by means of a Vilsmeier—Haak—Arnold reaction via the 1-chlorovin-amidinium 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).



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**-2**f** 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.



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

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

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entry	T _m [A] [°C]	entry	T _m [H] [°C]	T _g [H] [°C]	T _d [H] [°C]	E _{ox} ^a [V]
6a 6b 6c	157 166 167	2a 2b 2c	83 62 102	$-29 \\ -23 \\ \pm 0$	274 303 272	+0.86 +0.82 +0.87
6d 6e 6f	155 181 163	2d 2e 2f	104 109 83	+2 -21 -8	332 345 358	$+0.92 +1.17 +0.65^{b}$
6g ^c	157	$2\mathbf{g}^d$	20		305	+0.55

^{*a*} Measured toward the SCE, irreversible potentials. ^{*b*} Reversible potential. ^{*c*} 2-Morpholinothiophene-5-carboxylic acid.¹² ^{*d*} 2-Morpholinothiophene.

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-

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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 $T_{\rm g}$ s 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 TiCl₄

as reagent, according to the recently published method of M. Periasamy et al.¹⁶ (Scheme 4).



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

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