Grignard Reactions on *Ortho* Dicarboxylic Arene Derivatives. Synthesis of 1,3-Dithienylisothianaphthene Compounds

Rafaël H. L. Kiebooms, Peter J. A. Adriaensens, Dirk J. M. Vanderzande,* and Jan M. J. V. Gelan

Institute for Materials Research (IMO), Division Chemistry, Limburg University, Universitaire Campus, B-3590 Diepenbeek, Belgium

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1,3-Dithienylisothianaphthene (**10a**) is obtained through ring closure of 1,2-dithienoylbenzene (**7a**). The synthesis of **7a** has been accomplished based on a Grignard reaction by adding 2-thiophenemagnesium bromide to 1,2-di(*S*-(2-pyridinyl)) benzenedithioate (**6b**) to obtain **7a** in a yield of 95%. The use of **6b** avoids the formation of the corresponding 3,3-dithienyl-3*H*-isobenzofuran-1(3H)-one (dithienylphthalide, **8**). The same procedure is applied to obtain 1,3-dithienyl-4,5,6,7-tetradeuterioisothianaphthene (**10b**) and 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (**10c**). The synthesis of the 2,3-dithienoylpyridine (**12a**), 3,4-dithienoylpyridine (**12b**), and 2,3-dithienoylpyrazine (**12c**) however fails. The presence of nitrogen in the central ring system influences the result of the Grignard reaction. Possibly the free electron pair of the nitrogen interferes with the formation of a stable six-membered ring intermediate which is essential for the diketone formation.

1. Introduction

Conducting polymers have been the subject of intensive research for some time. The best known conducting polymers are poly(aniline), poly(*p*-phenylenevinylene), poly(pyrrole) (PP), and poly(thiophene) (PT). In the case of these polymers techniques have been developed to obtain good processability. Poly(isothianaphthene) (PITN) is another conducting polymer with most intriguing properties such as a low band gap of 1 eV and the ability to become transparent upon doping. However PITN has not yet found wide application in the development of electronic devices due to the lack of a simple polymerization route, leading to a processable material. The main problem should be attributed to the difficult accessibility of monomeric isothianaphthene compounds. Extensive work on isothianaphthene compounds has been accomplished by Cava et al.[1−3] From their work it appears that isothianaphthene monomers are relatively unstable and their synthesis is laborious. Although progress has been made on the development of a straightforward polymerization route to PITN,[4] it seems interesting to develop on the other hand synthetic procedures which lead to different types of monomeric isothianaphthene derivatives. These compounds should combine the interesting electronic properties of isothianaphthene with the possibility of enhancing stability and processability of the resulting polymer. The combination of the ITN unit with other aromatic heterocycles is an approach which is able to meet the requirements of enhanced stability and processability. Indeed, the control of the chemistry of for example PP and PT has made an important step forward during the last decade.[5−12] The most promising results in this field were obtained by McCullough et al.,[12] who were able to synthesize soluble alkyl-substituted and highly regioregular PT. Therefore, it is worthwhile to develop a new class of materials in which the already-demonstrated properties of PT are combined with the promising electronic properties of PITN. This class of polymers would consist of a well-defined combination of thiophene and isothianaphthene units. Moreover, since perfectly regioregular polymers[12] show superior electronic properties and while tailoring the bandgap is predicted to be easier in regular copolymers,[13−15] it is preferable to produce regular copolymers rather than random copolymers. In the case where the regularity of the copolymer is a direct result of the molecular structure of the monomer, we prefer to classify these materials as *formal* copolymers. The most obvious example of a *formal* copolymer is a polymer **1** in which the monomeric compound combines ITN unit as well as thiophene units. One interesting compound is 1,3-dithienylisothianaphthene (DTI, **10a**) in which two thiophene rings are combined with one isothianaphthene ring.[16,17] The totally symmetric structure of the monomer guarantees a high regularity in the copolymer structure.

The presence of thiophene rings on both sides of the ITN unit will favor the aromatic over the quinoid ground-state geometry. As far as the bandgap is concerned, a value in between those of PT and aromatic PITN is thus to be expected.[13,15,18] Moreover, the thiophene ring systems allows one to obtain easily processable polymers

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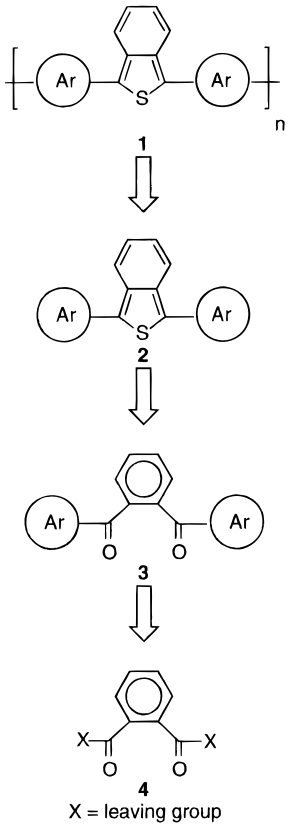
through, for instance, use of thiophenes with additional side chains. Certainly in the case of PT the incorporation of side chains is a technique which is now common use in improving solubility and therefore processability properties. Furthermore, **10a** can be used in the development of oligomers with tailored electronic properties. Recently[19−22] it was shown that one does not always need polymers to obtain electronic materials with outstanding properties. Even oligomeric compounds can meet the criteria for materials used in the preparation of advanced electronic devices. In the case of organic semiconducting materials based on oligomers, the solid-state properties are directly connected with these of the individual molecules and their spatial order. Recently it appeared to be possible to obtain devices with anisotropic properties[20,22] through control of the mesoscopic order of oligomers. The control of mesoscopic order is to a considerable extent influenced by the nature of substituents and end groups, a feature which can in its turn be controlled by a well-chosen synthetic route. Oligomeric compounds not only allow the obtention of materials with high purity but also allow easy control of the electronic properties. Moreover the structure of these compounds can readily be determined by a whole series a spectroscopic methods, facilitating thereby the unravelling of the correlation between the structure and the resulting electronic properties. Finally, oligomers present an additional advantage of allowing calculations[23] to be performed at a highly sophisticated level.

The most straightforward way to synthesize 1,3-diarylisothianaphthene derivatives **2** is through ring closure of *ortho* diketones **3** (Scheme 1) by means of P_4S_{10}[24] or Lawesson's reagent.[17,25] From literature[16,17] the preparation of these *ortho* diketones **3** appeared to be the major bottleneck to elaborate an efficient isothianaphthene synthesis. Although the use of Diels−Alder-type reactions[24,26,27] has been proposed, the use of this type of reaction for synthesis of a wide series of *ortho* diketone derivatives is rather limited. Since it is known that the Friedel−Craft-type reaction with phthaloyl dichloride **5a**[16,28] on thiophene results in the formation of 3,3-dithienylisobenzofuran-1(3*H*)-one **8** (Scheme 2), the use of Grignard-type reactions on *ortho* dicarboxylic arenes **4** to make *ortho* diketones is the only alternative.

In a Grignard reaction with 2-thienylmagnesium bromide as the Grignard reagent one can use different substrates. In literature the use of **5a**,[16,29] phthalic anhydride[30,31] and thiophthalic anhydride[32,33] has been reported in the synthesis of *ortho* diketones. However,

Scheme 1



the results of different authors appeared not to be entirely consistent with one another. Due to the inconsistency in literature data, we decided to revise the synthesis of *ortho* diketones in order to develop a convenient route to *ortho* diketones. Therefore we tested the results of Grignard reactions on the above series of substrates as well as on two new but no less interesting substrates, 1,2-di(*S*-phenyl)benzenedithioate (**6a**) and 1,2-di(*S*-(2-pyridinyl))benzenedithioate (**6b**). The latter compounds have a thioester functional group, which is reported to yield selectively ketones[34,35] from Grignard reactions.

Once an appropriate route to *ortho* diketones and thus **10a** had been developed, we investigated the application of this route in the synthesis of DTI derivatives (Scheme 1). Besides the synthesis of 1,3-dithienyl-4,5,6,7-tetradeuterioisothianaphthene (**10b**) and 1,3-dithienyl-4,5,6,7-tetrafluoroisothianaphthene (**10c**), the synthesis of different nitrogen-substituted derivatives **13a**, **13b**, and **13c** was attempted.

2. Results and Discussion

2.1 Synthesis of *Ortho* Diketones. As mentioned before, the bottleneck in the synthesis of **10a** was the preparation of the *ortho* diketone **7a**. We therefore first focused on the synthesis of this compound, as the synthesis of **10a** by ring closure with P_4S_{10}[24] or Lawesson reagent[17,25] is rather straightforward. For the synthesis of **7a** we investigated successively the Grignard reaction of 2-thienylmagnesiumbromide on **5a**, phthalic anhy-

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dride, thiophthalic anhydride and the two thioester compounds **6a** and **6b**.

2.1.1. Phthaloyl Dichloride. The investigation of the Grignard reaction on **5a** was based on the method of Jensen.[29] The reaction was performed by adding the thienylmagnesium bromide to a solution of **5a** in ether at a temperature of −78 °C. However, only a yield of about 10% was obtained, and the material contained a certain amount of colored matter which was very difficult to remove. Even the slow addition of the Grignard reagent to a solution of **5a** in THF at −78 °C or the use of a 1:2 toluene mixture[31] resulted in a very poor yield of the *ortho* diketone **7a** besides the formation of alcohols and many other side products. These results were later confirmed by Bäuerle et al.,[16] who did not succeed at all in obtaining **7a**. Apparently, two acid chlorides in the *ortho* position are too reactive toward this kind of nucleophilic substitution even at lower temperatures.

2.1.2. Phthalic Anhydride and Thiophthalic Anhydride. Another possible starting product in this reaction is phthalic anhydride. Since the reactivity toward a second nucleophilic substitution is seriously reduced after the opening of the anhydride ring system we performed the Grignard reaction at somewhat higher temperatures than usual. Therefore, we used refluxing solvent mixtures of toluene/ether in a ratio of 1:2, 1:3, and 4:1.[31] According to qualitative TLC analysis of the reaction mixtures, the best results were obtained in the solvent mixture with a ratio of 1:2 (boiling temperature of 58 °C). After purification by means of column chromatography a yield of 15% of the *ortho* diketone **7a** was obtained. However, a significant amount of **8** (29%) was also obtained. Performing the reaction at lower temperatures did not improve the yield of the *ortho* diketone **7a**.

As sulfur has better leaving group characteristics, we performed analogous reactions on thiophthalic anhydride. The synthesis of thiophthalic anhydride was carried out following the method of Reissert et al.[36] In analogy to the previous Grignard reaction on phthalic anhydride, the Grignard reaction was carried out in a refluxing 1:2 toluene/ether mixture. The work-up of the final reaction mixture was accompanied by considerable evolution of H_2S. However, the main reaction product appeared to be compound **8**. From a solid probe MS analysis (+CI mode) of the reaction products, obtained from a reaction carried out in pure THF solution, it appeared that monosubstituted thiocarboxylate is formed as an important intermediate. When diethyl ether at 0 °C is used as solvent a precipitate is formed during addition of the Grignard reagent. The yield of *ortho* diketone **7a** is higher than in the other cases (40%). When the reaction is carried out in diethyl ether at room temperature, one obtains a yield of about 60%. Apparently, lower temperatures favor the formation of monosubstituted intermediates. This indicates that the thiocarboxylate formed after the first attack by the Grignard reagent does not contain a suitable leaving group.

The specific structure of the isomer **8** was proved by means of IR-spectroscopy, the carbonyl group of γ-lactones absorbing at higher energy ($\nu = 1750$ cm^{-1}) than the one of the diketone **7a** ($\nu = 1630$ cm^{-1}). Moreover, ^{1}H NMR spectroscopy shows a coupling pattern of an asymmetric *ortho*-substituted benzene ring and the ^{13}C NMR spectra shows the chemical shift of an aliphatic quaternary carbon nucleus at 99.1 ppm. Compound **8** and **7a** were also carefully analyzed by means of 2D NMR techniques. In addition the structure of **8** was confirmed by the characteristic loss of CO_2 in mass spectroscopic studies.

2.1.3. 1,2-Di(*S*-phenyl) Benzenedithioate and 1,2-Di(*S*-(2-pyridinyl)) Benzenedithioate. Since **5a** is too reactive toward Grignard reactions and since phthalic anhydride and thiophthalic anhydride do not possess a very good leaving group, we investigated the use of a more convenient functional group, i.e. a thioester. A dithioester compound has two functional groups with a lower reactivity as compared to **5a**. Cardellicchio et al.[34] describe a highly efficient route to ketones through reaction of Grignard reagents with *S*-phenyl thioesters in the presence of iron catalysts. Another method for efficient synthesis of ketones is reported by Araki et al.[35] and is based on the use of *S*-(2-pyridinyl) thioesters. Therefore we have to synthesize the corresponding *S*-phenyl thioester **6a** and *S*-(2-pyridinyl) thioester **6b**.

Thus in a first approach for the synthesis of the *S*-phenyl thioester **6a**, **5a** was added slowly to a solution of thiophenol and triethylamine (TEA) in tetrahydrofuran (THF) according to the method of Araki et al.[35] (Scheme 2). This resulted however in the formation of two reaction products. Since both products possess the same molecular mass, we were dealing with two isomeric compounds. The first product is characterized by an IR absorption at 1670 cm^{-1} and the ^{1}H NMR spectrum shows a typical symmetric substitution of the benzene ring. The other product possesses an IR-absorption at 1770 cm^{-1}, a ^{1}H NMR spectrum showing a typical asymmetric substitution of the benzene ring, the presence of an aliphatic quaternary carbon nucleus at 99.1 ppm and the loss of CO_2 in solid probe MS analysis (+CI mode). From this spectroscopic data we can conclude that the first product should be the desired thioester **6a**. The second product, however, should possess a 3,3-bis(phenylthio)isobenzofuran-1(3H)-one structure **9**. Carefully monitoring the reaction as a function of time revealed that there occurs a conversion from **6a** to **9**. At room temperature this process takes a few days but at elevated temperatures the conversion is completed within an hour. Moreover when the reaction is carried out in the presence of an excess of thiophenol, **9** appeared to transform into two other products. The first one could be identified as being the phenyl disulfide based on mass spectroscopy and melting point (61 °C). The second product possesses an IR-absorption at 1770 cm^{-1}, the ^{13}C NMR spectrum indicates the presence of an aliphatic quaternary carbon nucleus at 86.4 ppm, and the ^{1}H NMR spectrum still showed the asymmetric substitution on the benzene ring. But at 6 ppm a new signal appeared with an integration corresponding with one hydrogen nucleus. All this spectroscopic data indicates the formation of 3-(phenylthio)isobenzofuran-1(3*H*)-one (**11**) in which one of the thiophenol groups is replaced by a hydrogen nucleus. The formation of disulfide in the presence of an excess of the corresponding thiol indicates that radical scavenging has taken place. Indeed it is known that thiols act as radical scavengers[37] with formation of the corresponding disulfide. Since the radical scavenging is accompanied with a proton transfer, a stable radical is formed at the 3-position of the structure of **9**. Indeed,

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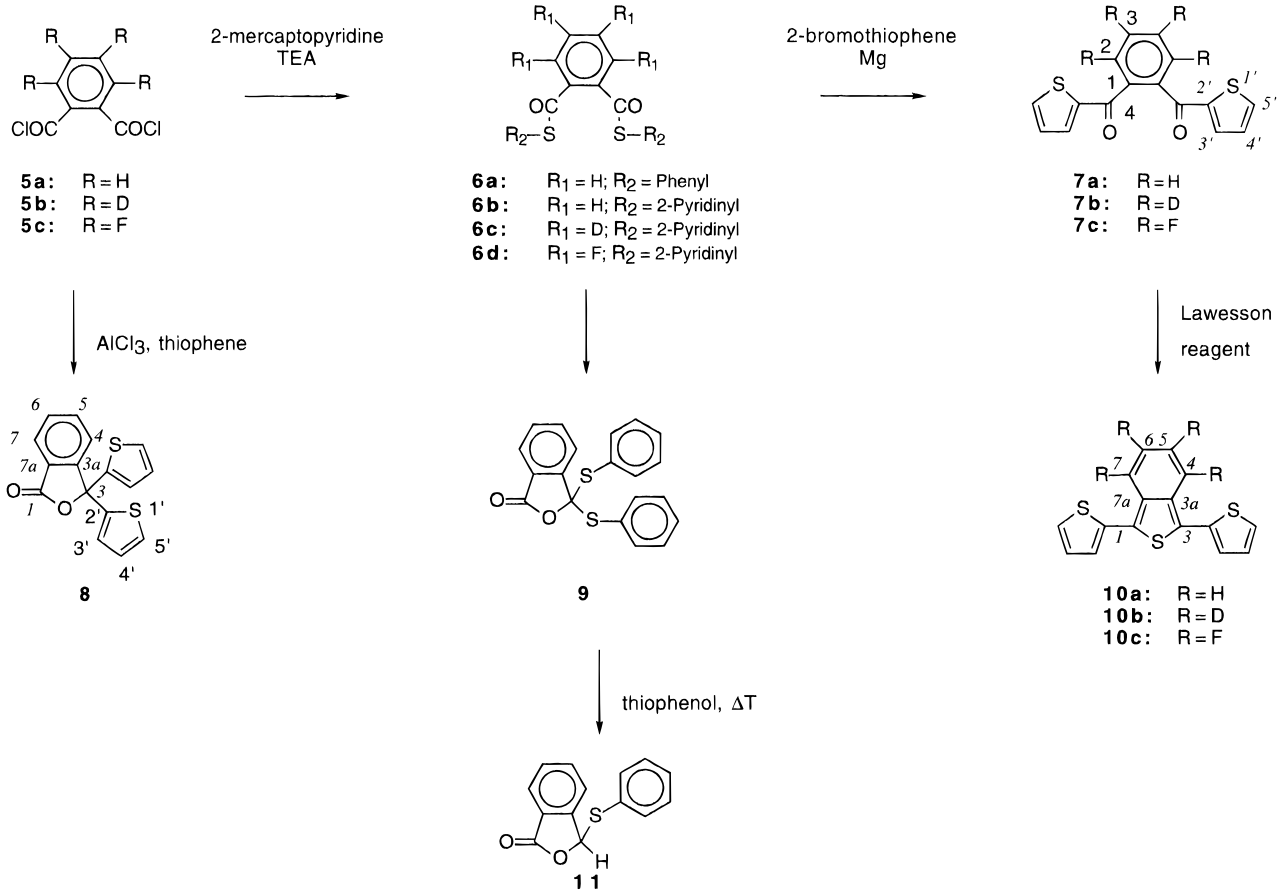
Scheme 2



the radical is not only stabilized by delocalization in the aromatic ring system but it is also stabilized by delocalization in the thiophenol group. This explains the replacement of the thiophenol group by a proton in presence of an excess of thiophenol. Starting from a solution of **9** in THF and heating it up in the presence of a large excess of thiophenol yielded an almost quantitative conversion into **11** and the formation of an equimolar amount of disulfide.

In order to obtain mainly the thioester **6a** we need therefore to work at lower temperatures with a slight deficiency of thiophenol. Moreover, since the reaction proceeds quite quickly one needs to stop this reaction at an early stage. Therefore, **5a** was added rapidly to a vigorously stirred solution of thiophenol and TEA in THF at 0 °C. When addition was completed, the reaction was immediately quenched by addition of an HCl-solution (1%). Since the lactone **9** is soluble in diethyl ether but not the thioester **6a**, purification can be done by simple crystallization from dichloromethane/diethyl ether, giving a yield of 77%. An alternative for this route is the method of Sheenan et al.[38] This method consists in adding **5a** dropwise at a temperature of 0 °C to thiophenol in a methanolate solution. The thioester **6a** precipitates from solution therefore preventing any isomerization to the lactone structure resulting in a yield of about 94%.

Since it appears that the process of lactone formation is thermodynamically favored, one may also expect this kind of intramolecular cyclization reaction to occur during Grignard reactions on compounds containing *ortho* carbonyl oxygen nuclei, as observed in the Grignard reaction on phthalic anhydride and thiophthalic anhydride.

Since we had control of the thioester synthesis, the next step consisted in performing the Grignard reaction in presence of iron catalysts. Therefore the Grignard reagent was slowly added at 0 °C to the thioester **6a** in a solution of THF in the presence of a catalytic amount of tris(acetylacetonate) iron(III). However this reaction did not result in the formation of the 1,2-dithienoylbenzene and a significant amount of **9** was isolated.

Since the use of **6a** did not yield **7a**, we used instead of **6a** the *S*-(2-pyridinyl) thioester **6b**.[39] This thioester was prepared according to the adapted method of Araki et al.[35] We did not succeed in preparing **6b** according to the method described by Sheehan et al.[38]

The high reactivity of *S*-(2-pyridinyl) thioesters toward Grignard reagents with selective formation of ketones was attributed to the formation of a stable six-membered intermediate which would prevent further reaction. The stable complex should in our case also prevent any intramolecular isomerization by "freezing" the intermediate in an organometallic complex (Figure 1). The final elimination occurs during acid work-up, causing the organometallic complex to break up. Thus the Grignard reagent was added slowly to **6b** in a solution of THF at 0 °C (Scheme 2). No precipitate was formed during reaction, allowing homogeneous mixing of the reaction products throughout the addition process. The reaction was finally quenched by addition of HCl (10%). After a

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(39) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95(14)*, 4763−4765.

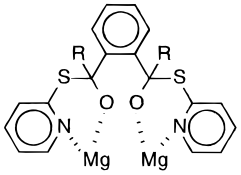


Figure 1. The formation of two six-membered complexes during the Grignard reaction on 1,2-di(*S*-(2-pyridinyl)) benzenedithioate.

classical work-up a yield of 95% of the *ortho* diketone **7a** was obtained. Eventually the product can be used in the next reaction without further purification.

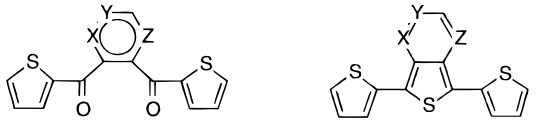
From these results it is clear that the use of thioesters in the synthesis of *ortho* diketones presents several important advantages. This *S*-(2-pyridinyl) thioester method is the first reported highly efficient and selective synthesis of *ortho* diketones. Moreover the synthesis of the thioester is straightforward and does not require laborious and time-consuming purifications.

2.1.4. Synthesis of Deuterated and Fluorinated *Ortho* Diketones. Since the deuterated **5b** and fluorinated **5c** phthaloyl dichloride derivatives are not commercially available, we have to start with the synthesis of the corresponding phthaloyl dichloride from the corresponding *ortho* dicarboxylic acid. Two methods were tested. The method using PCl_5 appeared to give better results as compared to the $SOCl_2$ method. The former gives a yield of around 90% for most of the *ortho* dicarboxylic compounds.

Next, the method as described in Scheme 2 was followed for the synthesis of the deuterated **6c** and fluorinated **6d** 1,2-dithienoyl benzene. The deuterated compound does not show an important difference as far as the chemical reactivity is concerned. Therefore it could be synthesized in a straightforward way according to the synthesis developed above.

Due to the high electronegativity of the fluorine nucleus, the reactivity of the carbonyl group is enhanced. For synthesis of the corresponding phthaloyl dichloride **5c** this is not a problem, but for the synthesis of the *S*-(2-pyridinyl) thioester **6d** it is. Preparation of **6d** based on the use of TEA as a base appeared not to be successful. **6d** could however be isolated through addition of **5c** to a sodium methanolate solution of 2-mercaptopyridine at −78 °C. The best results were obtained in a dry, oxygen- and moisture-free atmosphere as the product is much more reactive than the protonated derivative. The tetrafluoro diketone **7c** was obtained via the Grignard reaction by adding 2-thienylmagnesium bromide to a solution of **6d** in THF at 0 °C. The yield of 87% is comparable to the yield of **7a**.

2.2. Synthesis of Nitrogen Derivatives. From theoretical calculations on polymers[40,41] it appeared that the replacement of carbon atoms in the ITN ring system by nitrogen atoms influences the relative stabilities of the aromatic and quinoid forms. From analysis of the calculated electronic properties it appeared that there is a dependence not only on the nature of the fused rings but also on the positions of the nitrogens. The 4,5-diaza and 4,7-diaza polymers appeared to be quite promising: they present very small calculated energy gap values,



12a: X = N; Y = C; Z = C
12b: X = C; Y = N; Z = C
12c: X = N; Y = C; Z = N

13a: X = N; Y = C; Z = C
13b: X = C; Y = N; Z = C
13c: X = N; Y = C; Z = N

Figure 2. Compounds **12** and **13**.

0.27 and 0.18 eV, respectively, in their most stable geometric structure. Therefore, aza and diaza derivatives of ITN are the most interesting systems to be used in a *formal* copolymer. Since we established a convenient route toward the synthesis of *ortho* diketones, we investigated to what extent this method can be applied for the synthesis of aza and diaza derivatives of PITN. On the basis of our method we tried out the synthesis of dithienylthieno[2,3-*c*]pyridine (**13a**), dithienylthieno[3,4-*c*]pyridine (**13b**), dithienylthieno[2,3-*c*]pyrazine (**13c**) through the synthesis of the corresponding *ortho* diketones **12a**, **12b** and **12c** (Figure 2). An additional feature is that these compounds can be used to get an approximation of the spectroscopic characteristics of the corresponding aza and diaza ITN homopolymers.

2.2.1 Dithienylthieno[2,3-*c*]pyridine. By using the methods based on PCl_5 and $SOCl_2$ to synthesize the corresponding phthaloyl dichloride, 2,3-pyridinoyl dichloride (**14a**) was obtained in a yield of 90%. The synthesis of the *S*-(2-pyridinyl) thioester **15a** was performed using the TEA method with a yield of 68%. It should be noticed that **15a** is not soluble in THF or other solvents suitable for Grignard reactions. The only solvent appeared to be pyridine, but this is not a good Grignard solvent since the Grignard reagent readily decomposes.[42]

At first the Grignard reaction was carried out in the usual way in a solution of THF at 0 °C. However, the characteristic IR absorption at 1760 cm^{-1}, the presence of an aliphatic quaternary carbon signal at 86.8 ppm, and the loss of CO_2 in the mass spectra indicate the formation of a compound with the 3,3-dithienylfuropyridin-1(3*H*)-one **16a,b** structure in relatively high yield of 64%. Even carrying out the reaction at higher temperatures to enhance solubility did not solve the problem. Since we obtained almost a single pure compound, the question arises whether the pyridine nitrogen is situated at the carbonyl side **16a** or at the aliphatic side **16b** of the 3,3-dithienylfuropyridin-1(3*H*)-one compound (Scheme 3).

A detailed structure analysis based on the use of a combination of 2D ^1H-^{13}C heteronuclear correlation NMR experiments optimized for $J = 140$ Hz and $J = 8$ Hz helps to elucidate the structure of the obtained compound. The full chemical shift assignment has been carried out as on the previous compounds and is included as Supporting Information. The presence of a long-range correlation signal between C1 and H7 and the absence of a correlation signal between C3 and a pyridine proton indicate the nitrogen to be situated at the aliphatic side of the 3,3-dithienylfuropyridin-1(3*H*)-one compound. The reaction product therefore possesses structure **16b** (3,3-dithienylfuro[5,6-*c*]pyridin-1(3*H*)-one).

2.2.2 Dithienylthieno[3,4-*c*]pyridine. Since the synthesis of **12a** was not successful, we tried to perform the synthesis of the 3,4-pyridine derivative **12b**. Al-

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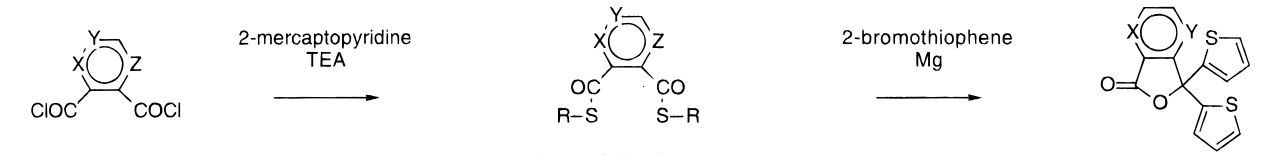
(41) Quattrocchi, C.; Lazzaroni, R.; Kiebooms, R.; Vanderzande, D.; Gelan, J.; Brédas, J. L. *Synth.Met.* **1995**, *69*, 691−692.

(42) Houben-Weyl; Nützel, K. *Houben-Weyl* **1993**, *Band 13/2a*, 54−75.

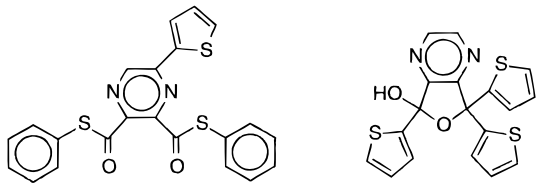
Scheme 3



14a: X = N; Y = C; Z = C
14b: X = C; Y = N; Z = C
14c: X = N; Y = C; Z = N

15a: X = N; Y = C; Z = C; R = Pyridinyl
15b: X = C; Y = N; Z = C; R = Pyridinyl
15c: X = N; Y = C; Z = N; R = Pyridinyl
15d: X = N; Y = C; Z = N; R = Phenyl

16a: X = N; Y = C
16b: X = C; Y = N
16c: X = N; Y = N



17 **18**

Figure 3. Compounds **17** and **18**.

though the 3,4-pyridinoyl dichloride (**14b**) could be obtained in a yield of 91%, we were not able to isolate **15b**. The reaction based on TEA resulted mainly in the formation of the 2-pyridine disulfide.

2.2.3 Dithienylthieno[3,4-*c*]pyrazine. In the synthesis of the pyrazinoyl dichloride (**14c**) a yield of only about 30% was obtained. This was mainly due to decomposition at higher temperatures. Also for the *S*-(2-pyridinyl) thioester **15c** syntheses, lower yields of about 40% were obtained as compared to other thioester syntheses. Again spectroscopic data indicated the formation of the lactone compound 3,3-dithienylfuro[2,3-*c*]pyrazin-1(3*H*)-one (**16c**; IR 1765 cm^{-1}, ^{13}C NMR 85.1 ppm) in the Grignard reaction. A possible solution for this problem is to make use of the fact that the pyrazine possesses two nitrogens. The idea was if one carries out the Grignard reaction on the *S*-phenyl thioester **15d** we can use both nitrogens of the pyrazine ring system for the formation of the organometallic complex. Unfortunately no diketone was formed in the Grignard reaction. Instead mainly two products **17** and **18** were isolated as shown in Figure 3, besides some unreacted *S*-phenyl thioester **15d**. The structure of compound **17** and **18** was confirmed by IR and mass spectroscopic data. Additional evidence for the structure of compound **17** and **18** was also obtained by a full chemical shift assignment based on 1D and 2D NMR homo- and heteronuclear correlation experiments.

2.3. Synthesis of DTI Derivatives by Ring Closure of *Ortho* Diketones. Finally the isothianaphthene core is formed through ring closure of the *ortho* diketone **7a** by means of P_4S_{10}[24] or Lawesson's reagent.[17] Both procedures were performed but the procedure based on the use of Lawesson's reagent appeared to be more efficient and easier to workup as compared to the use of P_4S_{10}. In the latter case one also has to counter the formation of important amounts of H_2S. The overall yield of **10a** based on this reaction scheme is 51%. This is the highest overall yield for the synthesis of **10a** reported so far. The overall yield of **10b** and **10c** are comparable to that of the protonated DTI.

The NMR data of **10b** confirms our assignment of C4/C7 and C5/C6 of the isothianaphthene ring. Indeed, the signals of deuterated carbon nuclei show a triplet because ^2H is a I = 1 nucleus. The difference of 0.5 ppm as compared to the protonated **10a** should be attributed to the presence of the isotope effect.

3. Conclusion

DTI derivatives could be of great interest for the development of semiconducting materials with tailor-made electronic properties as well as for spectroscopic and theoretical evaluation of structure−property relationships. Therefore our aim was to develop an efficient synthesis which makes it possible to prepare other DTI derivatives. Since an efficient method for the synthesis of **10a** was not available previously, we developed a highly specific and efficient synthesis route. In this method, the synthesis of *ortho* aryldiketones is the major bottleneck. A detailed evaluation of available starting compounds to be used in Grignard reactions was essential. For the synthesis of the 1,2-dithienoylbenzene (**7a**) we investigated successively the Grignard reaction of 2-thienylmagnesium bromide on **5a**, phthalic anhydride, thiophthalic anhydride, **6a** and **6b**. On the one hand **5a** appeared to be too reactive toward the reaction with 2-thienylmagnesium bromide, but on the other hand the reaction on phthalic anhydride and thiophthalic anhydride yielded, besides small to reasonable amounts of the **7a**, significant quantities of the isomeric **8**. The Grignard reaction on **6b** yielded selectively almost pure *ortho* diketone **7a**. This result was attributed to the formation of a stable six-membered organometallic complex. In an analogous reaction on **6a** according to the method of Cardellicchio et al.[34] the 3,3-di(*S*-phenyl-)isobenzofuran-1(3*H*)-one (**9**) was formed.

The synthesis of the deuterated **10b** and fluorinated **10c** DTI derivatives was successfully carried out. However, attempts of synthesizing the 2,3-pyridine **13a**, 3,4-pyridine **13b**, and 2,3-pyrazine **13c** derivatives failed at the level of Grignard reaction to obtain the 2,3-dithienoylpyridine **12a**, 3,4-dithienoyl pyridine **12b**, and 2,3-dithienoylpyrazine **12c**. The introduction of nitrogens in the aromatic ring system seemed to interfere with the formation of a stabilized six membered intermediate. In the case of the 2,3-pyridine the formation of the 3,3-dithienylfuro[5,6-*c*]pyridin-1(3*H*)-one structure **16b** is favored due to the difference in reactivity of both carbonyl functional groups caused by the inherent asymmetry of the ring system as a consequence of the presence of only one nitrogen.

Experimental Section

Synthetic Procedures. Solvents were dried and distilled prior to use. THF was distilled over Na/benzophenone, CH_3CN was distilled from CaH_2, and CH_2Cl_2 was distilled from P_2O_5. All compounds were crystallized or distilled prior to use. Products were purchased from Acros Chimica (previously Janssen Chimica). 3,4,5,6-Tetradeuteriophthalic acid (99.4 atom %) was purchased from Icon Services Inc. 3,4,5,6-Tetrafluorophthalic acid was purchased from Aldrich. All

reaction mixtures were dried over $MgSO_4$. All NMR spectra were recorded in $CDCl_3$, the shifts are reported in ppm relative to TMS unless specified otherwise.

Thiophthalic Anhydride. Phthalic anhydride (40 g, 0.27 mol) was thoroughly mixed with 80 g (0.33 mol) of $NaS_2{\cdot}9H_2O$. The resulting liquid was stirred for 5 h. Addition of 100 mL of water gave a yellow solution which was added slowly to 2 L of HCl (5%). When the addition was complete, the mixture was stirred for 1 h and filtered. The residue was dissolved in $CHCl_3$, washed with $NaHCO_3$ (1 M) and H_2O, and dried. After crystallization from $CHCl_3$/*n*-hexane, 35 g of white thiophthalic anhydride crystals was obtained (yield 78%): mp 105.5 °C; FTIR (KBr, ν, cm^{-1}) 1780, 1690, 1655; MS (EI, *m*/*z*) 164 (M^+), 104 ($M^+ - COS$), 76 ($M^+ - (CO)_2S$); ^1H NMR 7.82 (dd, 2, J = 2.9/5.1 Hz), 7.97 (dd, 2, J = 2.9/5.1 Hz); ^{13}C NMR 123.7 (CH), 135.0 (CH), 138.7 (C), 189.8 (C0).

***o*-Aryldicarbonyl Chlorides. A.** *o*-Aryldicarboxylic acid (0.0084 mol) and 0.0252 mol (5.25 g) of PCl_5 were slowly heated until 180 °C was reached (caution: HCl evolution at a temperature of about 60 °C). The mixture was kept for 2 h at 180 °C under vigorous stirring and then cooled to rt. The remaining PCl_5 was removed by filtration of the liquid into a vacuum distillation apparatus. The reaction flask was washed with 10 mL of toluene, and the solvent was filtered into the apparatus. Vacuum distillation yielded a liquid which was further used in the thioester synthesis.

B. A mixture of 18 mL of toluene and 0.1 mol of distilled $SOCl_2$ and 0.0084 mol of *o*-aryldicarboxylic acid were refluxed for 1.5 h. The solvent and remaining $SOCl_2$ were distilled off, and the product was further purified by vacuum distillation.

3,4,5,6-Tetradeuteriophthaloyl dichloride (5b): yield 1.46 g (84%); bp 204 °C (5 mmHg); IR (NaCl, ν, cm^{-1}) 1780, 1750, 1550.

3,4,5,6-Tetrafluorophthaloyl dichloride (5c): yield 2.2 g (94%); bp 180 °C (5 mmHg); IR (NaCl, ν, cm^{-1}) 1770, 1490; MS (CI, *m*/*e*) 275 (MH^+), 239; ^{13}C NMR 120.0, 143.6, 145.5, 161.5; ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to $CFCl_3$) −134.56, −144.82.

2,3-Pyridinoyl dichloride (14a): yield 1.56 g (91%); bp 140 °C (4 mmHg); IR (NaCl, ν, cm^{-1}) 3500, 3080, 1780, 1740, 1550; MS (CI, *m*/*z*) 204 (MH^+), 168 ($MH^+ - Cl$); ^1H NMR 7.72, 8.32, 8.84; ^{13}C NMR 127.0, 129.0, 138.6, 149.45, 153.0, 166.2, 167.4.

3,4-Pyridinoyl dichloride (14b): yield 1.56 g (91%); bp 145 °C (4 mmHg); IR (NaCl, ν, cm^{-1}) 3500, 2940, 2840, 1780, 1660, 1560; MS (EI, *m*/*z*) 205 (M^+), 169 ($M^+ - Cl$), 140 ($M^+ - CO$), 113 ($M^+ - COCl - CO$), 106 ($M^+ - COCl - Cl$), 78 ($M^+ - 2COCl$); ^1H NMR 7.62, 8.83, 8.97; ^{13}C NMR 121.9, 125.8, 141.7, 150.1, 153.0, 166.8, 168.0.

2,3-Pyrazinoyl dichloride (14c): yield 0.5 g (29%); bp 125 °C (4 mmHg); IR (NaCl, ν, cm^{-1}) 3500, 3040, 1780, 1730, 1550, 1530; MS (EI, *m*/*z*) 205 (M^+), 169 ($M^+ - Cl$),113 ($M^+ - COCl - CO$), 106 ($M^+ - COCl - Cl$), 78 ($M^+ - 2COCl$);^1H NMR 8.91; ^{13}C NMR 144.4, 146.8, 166.8.

1,2-(*S*-Phenyl)benzenedithioate (6a). A. A solution of 5 mL of TEA, 15 mL of THF, and 1.5 mL (0.0146 mol, 1.609 g) thiophenol was stirred for 15 min at 0 °C. A solution of 1 mL (0.0069 mol, 1.409 g) **5a** in 10 mL of THF was added. Immediately the reaction mixture was then worked up by adding 200 mL of HCl (1%). After extraction with $CHCl_3$ the combined fractions were washed with a NaOH (10%) solution and H_2O and finally dried. Crystallization from CH_2Cl_2/diethyl ether yielded 1.8 g (77%).

B. 5a (5.8 mL 0.04 mol) was added dropwise at 0 °C to 8.2 mL (0.08 mol) of thiophenol in a methanolate solution prepared by adding 1.74 g of Na to 50 mL of methanol. The precipitate was filtered off and washed with H_2O and ice-cold methanol: yield 13.2 g (94%); mp 130.3−130.5 °C; IR (KBr, ν, cm^{-1}) 1670 (ν_{COS}), 1570, 1210 (ν_{COSAr}), 1190 (ν_{COSAr}), 745(doublet); MS (EI, *m*/*z*) 351 (M^{+1}), 241 ($M^+ - SAr$), 213 ($M+ - COSAr$), 109 (SAr), 104 ($ArCO^+$), 76 (Ar^+); ^1H NMR 7.42, 7.52, 7.60, 7.82; ^{13}C NMR 191.6 , 137.1, 134.6, 131.6, 129.6, 129.2, 128.3, 127.4.

1,2-Di(*S*-(2-pyridinyl)) Benzenedithioate (6b). A solution of 5 mL of TEA, 50 mL of THF, and 3.3 g (0.030 mol) 2-mercaptopyridine was stirred for 15 min at 0 °C. A solution of 2.2 mL (0.015 mol) of **5a** in 50 mL of THF was added all at once. Immediately the reaction was then quenched by adding 200 mL of HCl (1%). After extraction with $CHCl_3$ the combined fractions were washed with 500 mL of NaOH (10%), 500 mL of $NaHCO_3$ (1 M) and 500 mL of water and dried. Crystallization from CH_2Cl_2/diethyl ether yielded 4.4 g (84%). mp 109.7 °C; IR (KBr, ν, cm^{-1}) 1680, 1655, 1420; MS (EI, *m*/*z*) 242 ($M^+ - S - Ar$), 214 ($M^+ - COS - Ar$); ^1H NMR 7.27, 7.61, 7.71, 7.74, 7.84, 8.59; ^{13}C NMR 123.7, 128.5 , 130.4, 132.0, 136.8, 137.2, 150.4, 151.3, 190.2.

1,2-Di(*S*-(2-pyridinyl)) 3,4,5,6-Tetradeuteriobenzenedithioate (6c). The same procedure as for **6b** was followed: yield 77%; IR (KBr, ν, cm^{-1}) 1680, 1650, 1570, 1560, 1535, 1450, 1420; MS (EI, *m*/*z*) 356, 246, 108, 78.

1,2-Di(*S*-(2-pyridinyl)) 3,4,5,6-Tetrafluorobenzenedithioate (6d). The reaction was carried out in a glovebox under nitrogen atmosphere at an ambient temperature of 10 °C due to the reactivity of the thioester and its sensitivity toward moisture. A sodium methanolate solution was prepared by adding at 0 °C 0.015 mol (0.35 g) Na to 50 mL of methanol and 0.0168 mol (1.86 g) of 2-mercaptopyridine and subsequently cooled down to −78 °C. A solution of 0.0084 mol (2.3 g) of **5c** in 25 mL of toluene was added dropwise under vigorous stirring. The precipitate was filtered off and rapidly washed with cold methanol (−78 °C) yield 1.53 g (43%); mp 71.5 °C decomposition; IR (KBr, ν, cm^{-1}) 1690, 1655, 1560, 1490; MS (EI, *m*/*z*) 424 (M^+), 333; ^1H NMR 7.30, 7.73, 8.60; ^{13}C NMR 121.7, 124.3, 130.2, 137.5, 142.2, 144.9, 149.7, 150.6, 184.0; ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to $CFCl_3$) −135.81, −147.31.

1,2-Dithienoylbenzene (7a). 2-Bromothiophene (4.5 mL, 46 mmol) in 50 mL of THF was added to 1.2 g (46 mmol) of Mg in 50 mL of THF. After stirring for 3.5 h, this solution was slowly added to 7.95 g (23 mmol) of **6b** in 150 mL of THF at 0 °C. After this solution was stirred for 30 min, 200 mL of HCl (10%) was added. The mixture was extracted with diethyl ether, and the combined fractions were washed with 500 mL of NaOH (10%), 500 mL of $NaHCO_3$ (1 M), and H_2O, and finally dried. A light brown product was obtained in a yield of 95%. This product can be used as such in further reactions. Crystallization from $CHCl_3$/*n*-hexane resulted in white crystals: mp 148−149 °C; IR (KBr, ν, cm^{-1}) 1620, 1585, 1570, 1510, 1410; MS (EI, *m*/*z*) 298 (M^+), 215 ($M^+ - COAr$), 187 ($M^+ - COAr$), 111 (COAr), 104, 76; ^1H NMR 7.03, 7.44, 7.60, 7.63, 7.70; ^{13}C NMR 128.0, 129.2, 130.6, 134.9, 135.1, 139.3, 144.0, 188.2. Anal. Calcd for $C_{16}H_{10}O_2S_2$: C, 64.4; H, 3.4. Found: C, 64.17; H, 3.28.

1,2-Dithienoyl-3,4,5,6-tetradeuteriobenzene (7b): yield 88%; IR (KBr, ν, cm^{-1}) 1620, 1545, 1510, 1410, 1350, 1330, 1280; MS (EI, *m*/*z*) 302, 273, 257, 219, 203, 191, 119, 111, 83.

1,2-Dithienoyl-3,4,5,6-tetrafluorobenzene (7c). The same procedure as for **7a** was followed using the following concentrations: 2 mL (20 mmol) 2-bromothiophene in 50 mL of THF was added to 0.5 g (20 mmol) of Mg in 50 mL of THF. This solution was added to 4.2 g (10 mmol) of crude **6d** in 150 mL of THF at 0 °C. Purification was performed by crystallization from $CHCl_3$/*n*-hexane or by column chromatography (silica, $CHCl_3$/*n*-hexane): yield 3.5 g (95%); mp 118 °C; IR (KBr, ν, cm^{-1}) 1620, 1510, 1470, 1410, 1375; MS (EI, *m*/*z*) 370 (M^+), 325, 287, 111, 83; ^1H NMR 7.09, 7.51, 7.74; ^{13}C NMR 123.5, 128.6, 136.2, 136.9, 141.6, 143.1, 144.8, 180.5; ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to $CFCl_3$) −136.68, −150.35. Anal. Calcd for $C_{16}H_6O_2F_4S_2$: C, 51.9; H, 1.6. Found: C, 51.39; H, 1.53.

3,3-Dithienylisobenzofuran-1(3*H*)-one (8). 5a (0.6 mL, 4 mmol) and 1.276 g of $AlCl_3$ were mixed thoroughly for 5 min at 0 °C. Slowly 1 mL (12 mmol) of thiophene in 20 mL of CH_2Cl_2 was added. The mixture was allowed to warm up to rt and was stirred for another 30 min. The mixture was poured in 100 mL of ice with 10 mL of HCl (37%). The product was extracted with ether, dried, and purified by column chromatography (*n*-hexane/$CHCl_3$). Crystallization resulted in white crystals with a yield of 0.76 g (64%): mp 99.6 °C; IR (KBr, ν, cm^{-1}) 1760, 1590, 1450, 1415; MS (EI, *m*/*z*) 298 (M^+), 253 ($M - CO_2$), 221, 111; ^1H NMR 6.94, 7.06, 7.29, 7.56, 7.66, 7.71, 7.90; ^{13}C NMR 86.3, 123.5, 124.8, 125.9, 126.8, 127.1,

127.3, 130.0, 134.6, 143.9, 151.9, 168.7. Anal. Calcd for $C_{16}H_{10}O_2S_2$: C, 64.4; H, 3.4. Found: C, 64.16; H, 3.29.

3,3-Di(*S*-phenyl)isobenzofuran-1(3*H*)-one (9). A solution of 5 mL of TEA, 15 mL of THF, and 1.5 mL (0.0146 mol, 1.609 g) of thiophenol was stirred for 15 min at room temperature. A solution of 1 mL (0.0069 mol, 1.409 g) of **5a** in 10 mL of THF was added. The mixture was stirred for another 2 h. HCl (200 mL, 1%) was then added. After extraction with $CHCl_3$ the combined fractions were washed with a NaOH (10%) solution and H_2O and finally dried. The product was purified by column chromatography (silica, $CHCl_3$/*n*-hexane) and crystallization from hexane to yield 1.9 g (79%): mp 101.9−102.3 °C; IR (KBr, ν, cm^{-1}) 1770, 1465, 1440; MS (CI and EI, *m*/*z*) 351 (M + 1), 306 (M − CO_2), 241 (M − SAr), 197 (M-CO_2 − SAr), 109 (SAr), 104 ($ArCO^+$), 76 (Ar^+); ^{1}H NMR 7.16, 7.26, 7.32, 7.38, 7.44, 7.64, 7.71; ^{13}C NMR 99.1, 123.3, 124.5, 125.8, 128.3, 128.7, 129.78, 129.82, 134.2, 136.4, 148.7, 167.1.

1,3-Dithienylisothianaphthene (10a). A. To a solution of 0.58 g (2 mmol) of **7a** in 40 mL of dried CH_3CN was added 1.7 g (6.1 mmol) of P_4S_{10} and 2.0 g (24 mmol) of $NaHCO_3$. After stirring for 4 h at a 30 °C, 50 mL of H_2O was added. The precipitate formed was filtered and dissolved in diethyl ether. After extraction of the remaining water solution with diethyl ether, the combined fractions were dried. Further fast purification was done through repeated crystallizations by adding *n*-hexane to a saturated $CHCl_3$ solution and combining the fractions containing **10a**. A final purification was performed through column chromatography (silica, *n*-hexane/$CHCl_3$) and crystallization from *n*-hexane/$CHCl_3$ resulting in fluorescent orange crystals (52%).

B. A mixture of 0.42 g (1.4 mmol) of **7a**, 0.4 g (1.4 mmol) of Lawesson reagent, and 50 mL of CH_2Cl_2 were stirred for 30 min at 30 °C. After evaporation of the CH_2Cl_2, 50 mL of ethanol was added and the mixture was refluxed for 20 min. Finally 100 mL of H_2O was added, and the product was extracted with diethyl ether. The combined diethyl ether fractions were washed with 500 mL of NaOH (10%) and 500 mL of H_2O and dried. The ether was evaporated, and the remaining solid was taken up in a minimum quantity of $CHCl_3$ and precipitated by adding a large quantity of *n*-hexane. The solid was filtered, and this procedure was repeated several times. All fractions containing almost pure product were then combined and subjected to final column chromatography (silica, *n*-hexane) (64%): mp 96−97 °C; IR (KBr, ν, cm^{-1}) 1520, 1215, 1180; MS (EI, *m*/*z*) 298 (M^+), 253, 221, 149, 132 (M^+ − 2Ar); ^{1}H NMR 7.13, 7.14, 7.34, 7.36, 7.94; ^{13}C NMR 121.5, 124.8, 125.5, 125.6, 126.5, 127.9, 135.4, 135.7; UV−vis (λ_{max}, ϵ) in *n*-hexane 426 (14 440), 283 (16 819), 220 (19 909).

1,3-Dithienyl-4,5,6,7-tetradeuterioisothianaphthene (10b): yield 64%; mp 95.6−96.0 °C; IR (KBr, ν, cm^{-1}) 1525, 1425, 1405, 1245; MS (EI, *m*/*z*) 302, 268, 257, 225, 151; ^{1}H NMR 7.14, 7.34, 7.37; ^{2}H NMR ($CHCl_3$, 400 MHz, in ppm relative to $CDCl_3$ at 7.24 ppm) 7.99, 7.18; ^{13}C NMR 121.1, 124.3, 125.5, 125.5, 126.4, 127.9, 135.2, 135.6.

1,3-Dithienyl-4,5,6,7-tetrafluoroisothianaphthene (10c). A mixture of 0.5 g (1.4 mmol) of **7c**, 0.4 g (1.4 mmol) of Lawesson's reagent, and 50 mL of CH_2Cl_2 were stirred for a maximum of 1 h at 45 °C. Working up was as for **10a**. Column chromatography (silica, *n*-hexane) yielded 0.48 g (95%): mp 184.6 °C; IR (KBr, ν, cm^{-1}) 2920, 1660, 1560, 1470, 1415; MS (EI, *m*/*z*) 370 (M^+), 203 (M^+ − 2Ar); ^{1}H NMR 7.11, 7.43; ^{13}C NMR 121.8, 127.8, 127.8, 127.9, 129.2, 132.7, 137.1, 139.1; ^{19}F NMR (fluorobenzene, 400 MHz, in ppm relative to $CFCl_3$) −145.68, −161.70; UV-vis (λ_{max}, ϵ) in *n*-hexane: 400 (12 656), 269 (16 372), 227 (23 159).

3-(*S*-Phenyl)isobenzofuran-1(3*H*)-one (11). A solution of 100 mL of TEA and 18 mL (263 mmol) of thiophenol was stirred for 15 min at room temperature. A solution of 6 mL (41.4 mmol) of **5a** in 50 mL of THF was added. The reaction mixture was stirred for 48 h at rt or 10 h at 60 °C and was then worked up by adding 200 mL of HCl (1%). After extraction with $CHCl_3$, the combined fractions were washed with NaOH (10%) and H_2O and finally dried. The product was purified by column chromatography (silica, $CHCl_3$/*n*-hexane) and crystallization from hexane to yield 8.7 g (87%): mp 103.5−103.8 °C; IR (KBr, ν, cm^{-1}) 1750 (ν_{COO} lactone), 1590, 1450, 1420; MS (EI, *m*/*z*) 242 (M^+), 133 (M^+ − SAr), 109 (SAr), 76 (Ar^+); ^{1}H NMR 6.71, 7.47−7.51, 7.69, 7.64, 7.77; ^{13}C NMR 86.4 , 123.4, 125.3, 126.1, 128.8, 129.0, 129.9, 130.2, 133.6, 134.2, 146.0, 169.0.

2,3-Di(*S*-(2-pyridinyl)) Pyridinedithioate (15a). A solution of 5 mL of TEA, 15 mL of THF, and 1.1 g (10 mmol) of 2-mercaptopyridine was stirred for 15 min at 0 °C. A solution of 5 mmol of **14a** in 10 mL of diethyl ether was added. Immediately the reaction mixture was then worked up by adding 200 mL of HCl (1%). After extraction with $CHCl_3$, the combined fractions were washed with 500 mL of NaOH (10%) and 500 mL of H_2O and finally dried. The product was purified by crystallization from CH_2Cl_2/diethyl ether to yield 1.2g (68%): mp 145 °C; IR (KBr, ν, cm^{-1}) 1675, 1560, 1550, 1440, 1410; MS (EI, *m*/*z*) 353 (M^+), 243 (M^+ − Spyr), 215 (M^+ − Spyr − CO), 187 (M^+ − Spyr − 2CO), 105 (M^+ − 2Spyr − CO), 78 (M^+ − 2Spyr − 2CO); ^{1}H NMR 7.24−7.31, 7.61, 7.67−7.79, 7.91, 8.57, 8.65, 8.80; ^{13}C NMR 123.6, 123.9, 127.2, 130.3, 130.7, 133.6, 135.8, 137.1, 137.4, 147.6, 150.4, 150.4, 150.5, 150.8, 151.7, 189.9, 189.9.

2,3-Di(*S*-(2-pyridinyl)) Pyrazinedithioate (15c). Synthesis was as described for **15a**: yield 0.8 g (46%); mp 137.6 °C; IR (KBr, ν, cm^{-1}) 1675, 1570, 1440, 1410, 1255; MS (EI, *m*/*z*) 244 (M − Spyr), 216 (M − COSpyr), 188, 156, 111, 78; ^{1}H NMR 7.26−7.32, 7.72−7.75, 8.60, 8.80; ^{13}C NMR 123.8, 130.4, 137.3, 145.8, 146.0, 150.6, 150.8, 188.7.

2,3-Di(*S*-Phenyl) Pyrazinedithioate (15d). Synthesis was as described for **15a**: yield 0.98 g (57%); mp 151.2−151.8 °C; IR (KBr, ν, cm^{-1}) 1670, 1525, 1450, 1420, 1370, 1250; MS (EI, *m*/*z*) 243, 215, 187, 160, 133, 109, 77, 65; ^{1}H NMR 7.40−7.45, 7.52−7.55, 8.76; ^{13}C NMR 126.4, 129.4, 129.9, 134.8, 145.7, 146.4, 189.6.

3,3-Dithienylfuro[5,6-*c*]pyridin-1(3*H*)-one (16b). Synthesis was as described for **7a** using **15a**: yield 4.4 g (64%); mp 142 °C; IR (KBr, ν, cm^{-1}) 3090, 3050, 1760, 1500, 1580, 1475, 1420, 1350, 1300, 1280; MS (EI, *m*/*z*) 299, 255, 222; ^{1}H NMR 6.96, 7.20, 7.32, 7.53, 8.22, 8.94; ^{13}C NMR 86.8, 118.8, 124.8, 126.9, 127.3, 127.5, 134.7, 142.0, 155.9, 166.9, 169.4.

3,3-Dithienylfuro[2,3-*c*]pyrazin-1(3*H*)-one (16c). Synthesis as described for **7a** using **15c**: yield 5.0 g (73%); mp 101.3 °C; IR (KBr, ν, cm^{-1}) 1765, 1530, 1460, 1415, 1370, 1335, 1280; MS (EI, *m*/*z*) 300, 256, 223; ^{1}H NMR 6.95, 7.17, 7.33, 8.88, 8.93; ^{13}C NMR: 85.1, 127.0, 127.6, 137.4, 140.8, 148.2, 149.1, 163.3, 164.4.

Grignard Reaction on 15d. Synthesis was as described for **7a** using **15d**.

Compound 17: yield 0.85 g (8.6%); mp 164.1−164.8 °C; IR (KBr, ν, cm^{-1}) 1680, 1540, 1500, 1470, 1430, 1410, 1370, 1350; MS (EI, *m*/*z*) 434, 325, 297, 133, 109; ^{1}H NMR 7.11, 7.45−7.50, 7.53−7.59, 7.62, 7.98, 9.14; ^{13}C NMR 127.0, 127.7, 128.9, 129.40, 129.44, 129.8, 129.9, 132.8, 133.5, 134.93, 134.97, 139.5, 141.0, 141.3, 142.9, 148.7, 189.6, 191.7.

Compound 18: yield 2.7 g (31%); mp 143.1−143.7 °C; IR (KBr, ν, cm^{-1}) 3200, 1440, 1420, 1370, 1350, 1280, 1250; MS (EI, *m*/*z*) 384, 285, 256, 162, 111.

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Supporting Information Available: NMR spectra and structure analysis and detailed NMR-data (58 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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