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Thieno[3,4-*b*]pyrazines: Synthesis, Structure, and Reactivity

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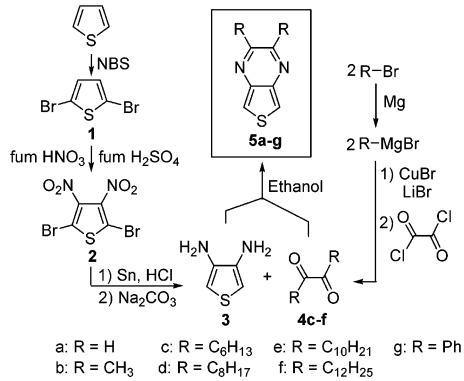
Abstract: A general synthetic route has been developed for the efficient preparation of 2,3-disubstituted thieno[3,4-*b*]-pyrazines. These methods eliminate problems in the preparation of the precursor 3,4-diaminothiophene and utilize α-diones prepared through the reaction of the appropriate organocuprates with oxalyl chloride. This combination allows the convenient preparation of thieno[3,4-*b*]pyrazine and its 2,3-disubstituted analogues (where substituent = methyl, hexyl, octyl, decyl, dodecyl, and phenyl) in high yield. Characterization of the structure and reactivity of this class of compounds is also described, including the results of structural, electrochemical, and pK_a studies.

Thieno[3,4-*b*]pyrazines have been shown to be excellent precursors for the production of low band gap conjugated polymers.[1−4] However, for these compounds to be fully utilized in such applications, a general synthetic route must be developed that allows access to a large number of different functionalities in the 2- and 3-positions. Such functionalities are necessary to tune and modulate the physical, electronic, and optical properties of the polymers.

The first report of a thieno[3,4-*b*]pyrazine was the synthesis of 2,3-diphenylthieno[3,4-*b*]pyrazine reported by Imoto and co-workers in 1957.[5] Binder and co-workers later reported a modified synthesis for the dimethyl analogue in 1981.[6] The first attempt at a general route to these compounds was published a year later by Outurquin and Paulmier.[7] Their approach applied modifications of the earlier methods to the preparation of thieno[3,4-*b*]pyrazine and its 2-substituted and 2,3-disubstituted analogues (where substituent = methyl or phenyl). This work, however, was still limited to commercially available α-diones and glyoxal for the formation of the pyrazine ring.

SCHEME 1



In 1992, Pomerantz and co-workers applied the methods of Outurquin and Paulmier to the synthesis of 2,3-dihexylthieno[3,4-*b*]pyrazine utilizing tetradecane-7,8-dione prepared by the oxidation of the corresponding alkyne.[1] Shortly thereafter, Kuzmany and co-workers also used these methods to prepare a series of 2,3-disubstituted analogues (where substituent = methyl, ethyl, hexyl, undecyl, tridecyl, and 2-thienyl).[2] However, while properties of the resulting polythieno[3,4-*b*]pyrazines were reported, neither author reported the synthetic details or any characterization of the monomeric precursors. In addition, the needed alkynes for this approach are typically not readily available.

Here we report a general synthetic route to 2,3-disubstituted thieno[3,4-*b*]pyrazines resulting from various improvements on the work of Outurquin and Paulmier combined with an optimization of the methods of Marchese and co-workers for the production of α-diones.[8] This synthetic route allows convenient access to the desired long-chain alkyl-functionalized precursors needed for the production of soluble polythieno[3,4-*b*]pyrazines and can be applied to the production of a variety of symmetrically substituted thieno[3,4-*b*]pyrazines. In addition, we include here the first full characterization of thieno[3,4-*b*]pyrazines, including the results of structural, electrochemical, and pK_a studies.

Synthesis. Thieno[3,4-*b*]pyrazine and its 2,3-disubstituted analogues can be readily synthesized from thiophene as shown in Scheme 1. While compounds **1** and **2** are commercially available, we have found it much more cost-effective and reliable to prepare these materials directly.

Compound **2** was readily produced by the nitration of **1** via fuming HNO_3 and H_2SO_4. Without the use of the fuming acids, only the mononitro product was produced. Likewise, an extended 3 h reaction time was required, as lesser times resulted in mixtures of mono- and dinitro-products. X-ray data show that the double bonds of **2** are slightly shorter than those of the parent thiophene,[9] while the C−C single bond is slightly elongated. This bond localization in **2** can be attributed to the donor−acceptor nature of the substituents as well as steric repulsion between the two NO_2 groups.

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Treatment of **2** with Sn and HCl both reduced the NO_2 functionalities and removed the Br protecting groups. As the reduction was carried out under acidic conditions, the isolated precipitate is the diammonium salt of **3** (**3**·$2H^+$ salt). In the procedure reported by Outurquin and Paulmier, the isolated **3**·$2H^+$ salt was purified by diethyl ether and acetone washes.[7] While this is necessary to remove impurities and residual HCl solution, it was found that if the salt was not adequately washed with ether first, the acetone wash resulted in complete product decomposition. This decomposition seemed to be initiated by the reaction of acetone with an ether-soluble impurity. Thus, it was difficult to determine when this reactive impurity was completely removed and it was safe to start the acetone wash. Working with various solvents, however, it was found that purification could be accomplished much easier using acetonitrile rather than acetone. Acetonitrile effectively removes the unwanted impurities but does not react with any remaining impurities as previously described for acetone.

In the original reports by either Imoto[5] or Binder,[6] the **3**·$2H^+$ salt is given the formula **3**·2HCl·$SnCl_4$, while Outurquin and Paulmier refer to it as a hexachlorostannate ($SnCl_6^{2-}$) diammonium salt.[7a] As $SnCl_4$ is a liquid at room temperature and usually adopts a six-coordinate geometry in the presence of additional ligands,[10] all of these formulations seem to refer to $SnCl_6^{2-}$ counterions. Elemental analysis of the isolated **3**·$2H^+$ salt, however, does not agree with a simple $SnCl_6^{2-}$ salt. In addition, the corresponding yield of the free base **3** is also not consistent with such a composition. These observations indicate that the **3**·$2H^+$ dication is present in higher quantities than would be consistent with the mass ratio of a pure $SnCl_6^{2-}$ salt. As the solution from which the salt precipitates contains roughly 4 times the amount of Cl^- compared to $SnCl_6^{2-}$, we believe that the isolated salt consists of a mixture of Cl^- and $SnCl_6^{2-}$ counterions with the general composition $[\mathbf{3}\cdot 2H^+]_x[SnCl_6^{2-}]_{(x\ -\ 1/2y)}[Cl^-]_y$ and therefore has a lower molecular weight than a pure $SnCl_6^{2-}$ salt. Attempts to determine the exact ratio of Cl^- to $SnCl_6^{2-}$ have been unsuccessful, as the ratio seems very dependent on the exact conditions during the salt precipitation and can change from one isolation to the next. For this reason, the free base **3** was always isolated prior to further reaction in order to determine an accurate molar quantity.

With the exception of glyoxal, 2,3-butanedione, and benzil, the α-diones necessary for the condensation with **3** to produce the desired thieno[3,4-*b*]pyrazines **5a**−**g** are not commercially available. While Pomerantz[1] and Kuzmany[2] had previously utilized symmetric alkynes as precursors to the required α-diones, a more direct synthetic approach was desired. Such an approach was reported by Marchese and co-workers for the preparation of symmetrical α-diones from oxalyl chloride.[8] However, while the procedure was fairly direct, the yields reported by Marchese could not be achieved due to the production of a large amount of homocoupled alkane byproduct. Marchese points out that lower temperatures (i.e., −78 °C) are required for the production of dialkyl α-diones in order to reduce such homocoupling, but even under such conditions, isolated yields were still only ∼10−20%. In this process, it was found that in order to adequately inhibit the homocoupling side reaction, the temperature must be very carefully controlled. For example, both the conversion of the Grignard reagent to the organocuprate and its subsequent reaction with the oxalyl chloride are exothermic. Thus, even with an initial temperature of −78 °C, it is quite easy to achieve temperatures from −40 to −30 °C during the various reaction steps and favor homocoupling during these periods. By cooling the mixture to even lower initial temperatures (−100 °C), however, and by adding the remaining reagents slowly over time, it was possible to keep the reaction mixture below −70 °C at all times. Such temperature control minimized unwanted homocoupling and resulted in α-dione yields of 70−90%.

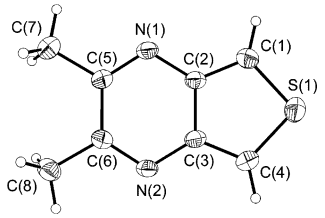

FIGURE 1. Ellipsoid Plot of 2,3-Dimethylthieno[3,4-*b*]pyrazine.

Condensation of **3** with the α-diones readily occurred at room temperature in an ethanol solution. While previous methods utilized short periods of heating (i.e., 50−70 °C for 10−15 min),[7b] it was found that by allowing the reaction to run at room temperature for longer periods of time, unwanted polymerization reactions were reduced and the thieno[3,4-*b*]pyrazines were recovered in higher yields. The initially isolated products were all relatively free of impurities, and analytical samples could be prepared by either recrystallization or chromatography.

Structure. X-ray quality crystals of **5b** could be grown by the slow evaporation of acetonitrile solutions, and the resulting crystal structure is shown in Figure 1. Selected bond angles and distances for **5b**, thiophene, and pyrazine are given in Table 1. Comparing the bond lengths of **5b** with the gas-phase distances of thiophene and pyrazine,[9] it can be seen that the thiophene ring of **5b** is nearly identical to the parent thiophene. The pyrazine portion of **5b**, however, shows some bond fixation in comparison to the parent pyrazine. For example, while the delocalized structure of pyrazine results in four equivalent C−N bonds, the pyrazine ring of **5b** exhibits elongation of the thiophene−N bonds and shortening of the exterior C−N bonds. In fact, the bond lengths of these exterior C−N bonds (i.e., C(5)−N(1) = 1.308 Å) are very close to the 1.28 Å length of localized C=N bonds.[11] In addition, the C(5)−C(6) unit separating these C=N units is also greatly elongated in comparison to pyrazine. Thus, **5b** can be viewed to be more similar to a diimine-capped thiophene than a truly delocalized structure.

The only previous crystal data for a thieno[3,4-*b*]-pyrazine were for the mixed trimer 2,3-dimethyl-5,7-di-(2-thienyl)thieno[3,4-*b*]pyrazine[3a] (**6**). Selected bond angles and distances for trimer **6** are given in Table 1. As seen

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TABLE 1. Experimental Geometrical Parameters of 2,3-Dimethylthieno[3,4-*b*]pyrazine (5b), Thiophene, Pyrazine, and 2,3-Dimethyl-5,7-di(2-thienyl)Thieno[3,4-*b*]pyrazine (6) and Calculated Parameters of Thieno[3,4-*b*]pyrazine (5a)

parameter	**5b**	**6**[a]	**5a** (calcd)[b]	**5a** (calcd)[c]	**5a** (calcd)[d]	thiophene[e]	pyrazine[e]
S(1)−C(1)	1.691	1.719	1.706	1.70	1.67	1.714	
C(1)−C(2)	1.372	1.407	1.384	1.36	1.38	1.370	
C(2)−C(3)	1.427	1.418	1.442	1.45	1.47	1.423	1.403
C(2)−N(1)	1.377	1.371	1.378	1.41	1.40		1.339
N(1)−C(5)	1.308	1.301	1.310	1.30	1.31		1.339
C(5)−C(6)	1.460	1.469	1.433	1.45	1.47		1.403
C(5)−C(7)	1.495	1.503					
C(1)−S(1)−C(4)	94.27	95.03		92.8	95.3	92.17	
S(1)−C(1)−C(2)	110.52	108.89		111.7	110.9	111.47	
C(1)−C(2)−C(3)	112.44	113.86		111.9	111.4	112.45	
N(1)−C(2)−C(3)	121.35	121.35		120.4	121.1		122.2
C(5)−N(1)−C(2)	116.05	116.21		116.3	115.5		115.6
C(6)−C(5)−N(1)	121.51	122.22		123.3	123.4		122.2
N(1)−C(5)−C(7)	117.60	118.46					

[a] From ref 3a. [b] From ref 12a. [c] From ref 12b. [d] From ref 12c. [e] From ref 9.

TABLE 2. Electrochemical Data for a Series of 2,3-Disubstituted Thieno[3,4-*b*]pyrazines[a]

	oxidation	reduction	
R	E_p[a], V	$E_{1/2}$, V	ΔE, mV
H	1.55		
CH_3	1.33	−2.04	85
C_6H_{13}	1.35	−2.01	150
C_8H_{17}	1.35	−1.99	130
$C_{10}H_{21}$	1.33	−1.99	140
$C_{12}H_{25}$	1.35	−1.96	130
Ph	1.27	−1.27	300

[a] All potentials are vs Ag/Ag^+. Voltammetric data were measured in millimolar argon-sparged CH_3CN solutions with 0.1 M $TBAPF_6$ as a supporting electrolyte.

in the structure of **5b**, trimer **6** also exhibits the same bond fixation in the pyrazine ring with bond lengths closely approximating that of **5b** and a C=N bond length of 1.301 Å. As might be expected, however, the central thiophene ring of trimer **6** differs significantly from **5b** due to conjugation effects with the two thienyl endgroups.

In addition to the experimental data, various calculated structures of the parent **5a** have been reported (Table 1). The first calculated structure was reported by Schneller and co-workers in 1976 and was limited to the bond length determinations using the CNDO/2 method.[12a] More complete calculations were then later reported by Marynick and co-workers[12b] using the PRDDO method and by Armand and co-workers using the MNDO method.[12c] All three calculated structures actually predicted the bond localization of the pyrazine ring quite well with an agreement of ±0.008 Å for the C=N bond lengths. The studies also modeled the thiophene ring fairly closely, with the major deviation being that all studies predicted an elongation of the C−C bond fused between the two heterocyclic rings, which was not seen in the structure of **5b**. In this case, the calculations predicted that both of the C−C bonds within the pyrazine ring were of equal length, rather than the asymmetric structure shown by the X-ray data.

Electrochemistry. The electrochemical data of **5a**−**g** are given in Table 2, and a representative cyclic voltammogram is shown in Figure 2. As expected for thiophene derivatives, **5a**−**g** exhibit a well-defined irreversible oxidation presumably corresponding to the formation and rapid coupling of thiophene-based radical cations ($\tau < 10^{-5}$ s), thus leading to oligomeric and polymeric species.[13,14a] For the series **5b**−**f**, the peak oxidation potentials (E_p[a]) are fairly consistent and occur at ∼1.35 V vs Ag/Ag^+. In the case of **5a**, the compound does not benefit from the electron donation of the alkyl groups and thus undergoes oxidation at a slightly higher potential. In contrast, **5g** exhibits the lowest oxidation (1.27 V) due to the partial overlap of the thieno[3,4-*b*]pyrazine π-system with that of the phenyl substituents. Overall, the oxidations of **5a**−**g** occur at much lower potentials than the ≳2 V of typical thiophenes.[14] These lower potentials can be attributed to the increased conjugation of the fused-ring compound and agree well with the oxidation potentials of other analogous fused-ring thiophene systems (1.1−1.5 V).[14b]

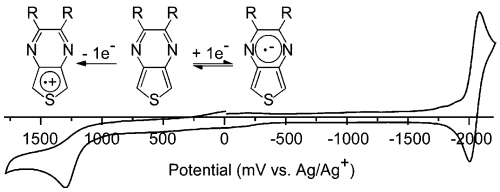

FIGURE 2. Cyclic Voltammogram of 2,3-Dimethylthieno[3,4-*b*]pyrazine (**5b**).

In addition to the thiophene-based oxidation, a quasi-reversible reduction is also exhibited at approximately −2.0 V. This observation agrees well with the previously reported electrochemical study of the reduction of **5b** by Armand and co-workers, which showed that this redox wave corresponds to the one-electron reduction of the pyrazine ring.[12c] In comparison to the previous oxidations, there is slightly more variation in the half-potentials ($E_{1/2}$) of the reductions with the potentials decreasing slightly with increasing substituent chain length. The main exception to this trend is **5a**, which does not exhibit a reduction. In this case, it is possible that the reduction

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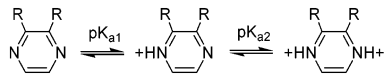
TABLE 3. pK_a Data for Pyrazines, Quinoxalines, and Thieno[3,4-*b*]pyrazines



compound	pK_{a1}	pK_{a2}
pyrazine[a]	0.57	−5.51
2-methylpyrazine[a]	1.41	−4.89
2,3-dimethylpyrazine[a]	2.24	−4.17
quinoxaline[b]	0.56	
2-methylquinoxaline[b]	0.95	
thieno[3,4-*b*]pyrazine (**5a**)	0.55	
2,3-dimethylthieno[3,4-*b*]pyrazine (**5b**)	1.66	−1.29

[a] From ref 16. [b] From ref 15a.

occurs just outside the solvent potential window of the acetonitrile. In addition to this first reduction, Armand and co-workers showed that by scanning to more negative potentials (ca. −2.4 V), the pyrazine ring of **5b** could be irreversibly reduced to produce the corresponding 1,4-dihydro derivative.[12c]

pK_a Studies. Spectrometric pH titrations of compounds **5a** and **5b** were carried out in order to quantify the basicity of the pyrazine nitrogens. The pK_a values determined from these studies are given in Table 3, along with the corresponding values for pyrazine, quinoxaline, and their methyl derivatives.

Typically, pyrazines and their derivatives are relatively weak bases. For example, the first protonation of pyrazine occurs with a pK_a of 0.57 in comparison to the much more basic pK_a of pyridine at 5.23. The lower basicity of pyrazine relative to that of pyridine is due to the strong inductive and mesomeric effects of the sp^2 nitrogen para to N(1).[15] In addition, the annulation of benzene rings to these aromatic bases generally only causes a small change in basicity.[15a] Thus, as seen in Table 3, the pK_a of quinoxaline is essentially the same as that of pyrazine.

The basicity of **5a** agrees well with that of both pyrazine and quinoxaline, giving a pK_a value of 0.55 for the first protonation (pK_{a1}, Table 3). Thus, while the structural data above indicate bond fixation within the pyrazine ring, the effect of the para nitrogen can still be effectively communicated, resulting in a pK_a typical of pyrazine. As expected, the effect of the fused thiophene ring is similar to a fused benzene ring and thus has little effect on the basicity. Following the initial protonation of **5a**, the UV−vis spectra show a third species forming at ∼pH 0. However, even in 12 M HCl, very little of this third species was present at equilibrium and the pK_a for the second protonation could not be reliably determined. This is hardly surprising, as the analogous pK_a values of pyrazines have been determined to be ca. −5 (Table 3).

In comparison to **5a**, the methyl analogue **5b** exhibits increased basicity and a pK_{a1} value of 1.66. This increased basicity with added methyl groups is typical for pyrazines (Table 3). The increased basicity is due to the electron-donating effect of the methyl moiety and is additive (∼0.84 pH units/methyl group).[15b,16] For quinoxaline, a similar methyl group-induced increase in basicity is seen but to a lesser extent (∼0.39 pH units).[15a] Assuming that the methyl group effect is also additive for the thieno-[3,4-*b*]pyrazines, this would correspond to an increase of ∼0.55 pH units/methyl moiety. Thus the methyl group effect for the thieno[3,4-*b*]pyrazines falls approximately halfway between that of pyrazines and quinoxalines. It is possible that the larger π-systems of the thieno[3,4-*b*]-pyrazines and quinoxalines result in the diminished effect of the methyl groups in comparison to that of pyrazine.

As with **5a**, a third protic species of **5b** can be seen at low pH. In this case, however, the formation of this species occurs under less acidic conditions and is the predominate species in 12 M HCl. The pK_a value determined for this second protonation is −1.29, much more basic than the corresponding value of −5.51 for pyrazine (Table 3). Unfortunately, the pK_{a2} values for quinoxaline or its methyl analogue have not been determined. However, one could make the argument that the larger π-system of the fused-ring systems facilitates a greater delocalization of the cation's positive charge in comparison to pyrazine, thereby diminishing the electrostatic barrier to the second protonation. While α-protonation of the thiophene ring is also possible, this typically promotes substitution and/or polymerization. In addition, Cook and co-workers[17] have shown that α-protonation of 2,5-di-*tert*-butylthiophene occurs with a pK_a of −10.16. Thus α-protonation is expected to be much less favorable than the protonation of the second pyrazine nitrogen. It has also been shown by others that protonation of the sulfur heteroatom is even less favored than α-protonation.[17a]

In conclusion, 2,3-difunctionalized thieno[3,4-*b*]pyrazines can be prepared simply and efficiently via the room-temperature condensation of **3** and an appropriate α-dione. In turn, the α-diones can be conveniently prepared from the reaction of alkylcuprates with oxalyl chloride. The resulting thieno[3,4-*b*]pyrazines exhibit the characteristics and reactivity of the parent heterocycles, although somewhat modified by the increased π-conjugation, as might be expected.

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Supporting Information Available: Experimental details for the synthesis and characterization of **1**−**5** and 2,3-dimethylthieno[3,4-*b*]pyrazine·2HCl, spectroscopic data and global analysis results used in the pK_a determinations, and full crystallography data for compounds **2** and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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