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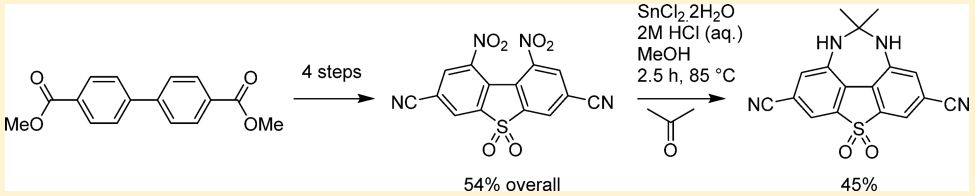
Synthesis of Tetracyclic 2,3-Dihydro-1,3-diazepines from a Dinitrodibenzothiophene Derivative

Stephanie Montanaro,[†,‡] Iain A. Wright,*[,‡] Andrei S. Batsanov,[†] and Martin R. Bryce*[,†]

[†]Department of Chemistry, Durham University, Durham, DH1 3LE, United Kingdom
[‡]Department of Chemistry, Loughborough University, Loughborough, LE11 3TU, United Kingdom

Supporting Information



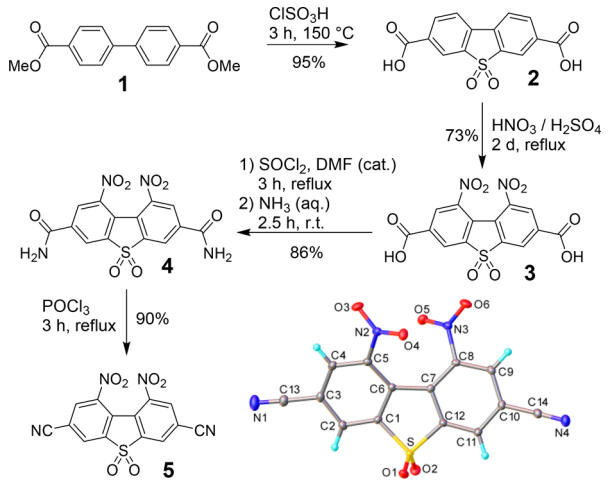
ABSTRACT: Triply fused 1,3-diazepine derivatives have been obtained by acidic reduction of rotationally locked and sterically hindered nitro groups in the presence of an aldehyde or ketone. The nitro groups are sited on adjacent rings of a dicyanodibenzothiophene-5,5-dioxide, which also displays fully reversible two-electron-accepting behavior. The synthesis, crystallographically determined molecular structures, and aspects of the electronic properties of these new molecules are presented.

Developing new routes to underexplored heterocyclic motifs is a fundamental driving force in organic chemistry and is essential to identifying new structures of medicinal or technological value. Diazepines are of major pharmaceutical importance.[1−3] 1,2-Benzodiazepines and 1,4-benzodiazepines in particular comprise entire classes of drugs, including the antianxiety medications tofisopam (strictly a 2,3-diazepine) and diazepam.[4−8] 1,3-Diazepines, and the saturated analogues 1,3-diazepanes, are less prevalent; however they have been studied as HIV protease inhibitors,[9−14] as anticancer[15−20] and antiviral agents,[15,21−28] and also as *N*-heterocyclic carbene ligands.[29,30] In comparison with 1,2- and 1,4-diazepines, routes to 1,3-diazepines are less clearly established. Since the last comprehensive survey of their synthesis[31] only a handful of new synthetic approaches have been reported for monocyclic,[32−35] singly[36−39] or doubly ring-fused 1,3-diazepines.[40−49]

In this work, the introduction of sterically hindered nitro groups at the 1- and 9-positions of a dibenzothiophene-5,5-dioxide derivative provides access to a new two-electron-accepting molecule, which is a precursor to luminescent four-ring-fused 2,3-dihydro-1,3-diazepines **6**−**8** using facile protocols in synthetically viable yields. To our knowledge, these molecules represent the first examples of tetracyclic 1,3-diazepine derivatives.

The synthesis of the new dibenzothiophene-5,5-dioxide acceptor is shown in Scheme 1. Simultaneous cyclization and acidic hydrolysis of dimethyl biphenyl-4,4′-dicarboxylate **1** was achieved in refluxing chlorosulfonic acid according to the procedure of Olkhovik et al. to produce diacid **2**.[50] In the same report, mononitration of **2** at the 1-position was performed; therefore, by using the more concentrated fuming nitric acid and extending the reaction time, dinitration was achieved to produce 1,9-dinitrodibenzothiophene-5,5-dioxide-3,7-dicarboxylic acid **3**. A byproduct containing a nitro group in the 2-position was reported for the mononitration;[50] however, we did not observe this during our dinitration process. Finally, the carboxylic acid groups of **3** were easily converted to nitriles using standard procedures. Reaction of **3** with an excess of refluxing $SOCl_2$ and a catalytic amount of *N*,*N*-dimethylformamide (DMF) gave the presumed diacyl chloride derivative,

Scheme 1. Synthesis of the New Acceptor 5 and Its X-ray Molecular Structure



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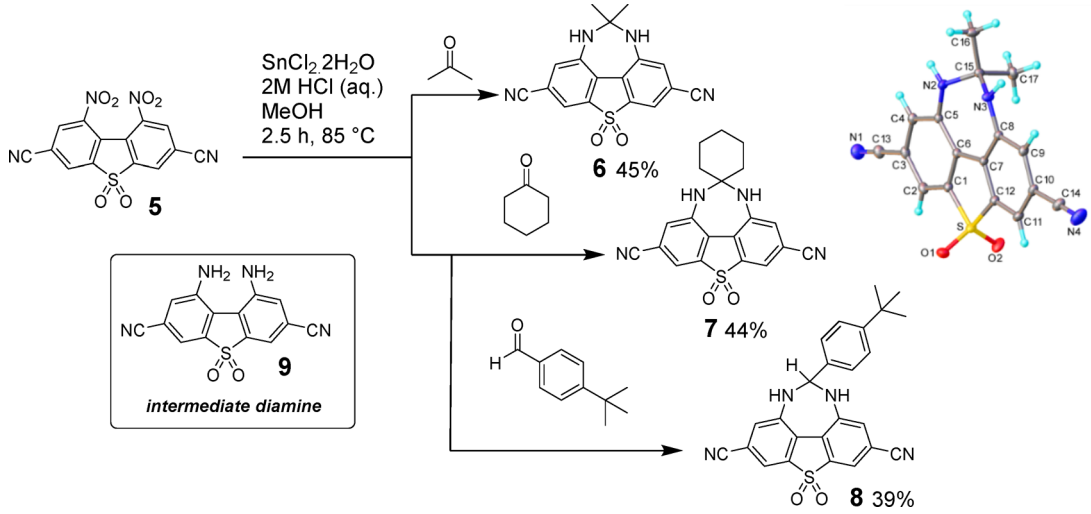
Scheme 2. Synthesis of Tetracyclic 1,3-Diazepines 6, 7, and 8 from 5 via Intermediate Diamine 9 and the X-ray Molecular Structure of 6



which was reacted immediately with aqueous ammonia to produce the diamide derivative **4**, which had a low solubility. Compound **4** was then dehydrated with $POCl_3$ to give **5**. Each step in Scheme 1 is straightforward to perform, relying upon simple precipitation and filtration to isolate products. The overall yield is 54% for the five-step sequence to compound **5**.

Considerable twisting of the aromatic skeleton of **5** occurs due to a combination of steric hindrance and repulsive electronic effects between the nitro groups. Relief of this ring strain should be a useful driving force in exploiting the reactivity of these nitro groups toward producing new heterocycles. Indeed, reduction of the nitro groups of **5** in the presence of aldehydes or ketones provides convenient access to the brightly colored 2,3-dihydro-1,3-diazepines **6**–**8**, featuring alkyl or aromatic substituents at the 2-position, via the diamine **9** (Scheme 2).

Acidic reduction of **5** using $SnCl_2{\cdot}2H_2O$ in the presence of acetone provided the *N*,*N*′-isopropylidene-2,3-dihydro-1,3-diazepine derivative **6**. The modest yield (45%) is offset by the straightforward practical protocol. To confirm the intermediacy of diamine **9** in this process, a separate experiment was performed, in which **9** was isolated, albeit in only 14% yield, and then cyclized in acidic acetone to provide **6** in 78% yield. The one-pot approach is, therefore, much more expedient than performing the reduction and cyclization sequentially, due to difficulties in isolating diamine **9**. Analogous one-pot reactions using cyclohexanone and 4-*tert*-butylbenzaldehyde gave **7** and **8**, respectively, in 44% and 39% yields.

We note that electrochemical reduction of 2,2′-dinitrobiphenyl in the presence of aldehydes and ketones has previously been used to produce 1,3-diazepines.[51] However, the reaction conditions reported above for converting **9** into **6** did not work with 2,2′-dinitrobiphenyl; no diazepine was isolated, and the only major product identified was 2,2′-diaminobiphenyl. This agrees with a previously reported high-yielding, tin-mediated, reduction of this[52] and related compounds.[53,54] We are aware of one example of a reductive cyclization of a 2,2′-dinitrobiaryl using $SnCl_2$ and an identical reaction stoichiometry to the present work, which resulted in trace (5%) benzo[*c*]cinnoline formation.[55] These results indicate that the structurally enforced proximity of the two amino groups in **9** is required for efficient reductive cyclization.

The diazepines **6**–**8** were brightly colored and emissive in both the solid state and in solution, unlike the precursor **5**, which is nonemissive. Absorption and emission spectra in acetonitrile are shown in Figure 1 and summarized in Table S1.

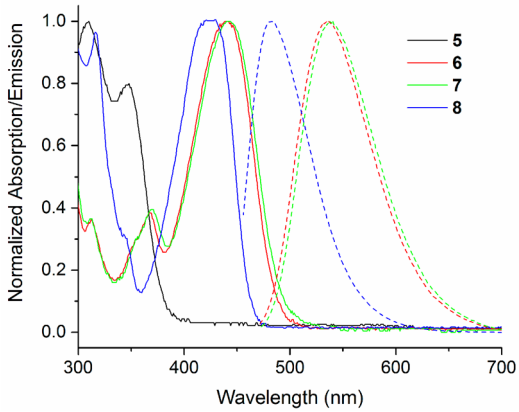


Figure 1. Absorption (solid line) and emission spectra (dashed line) for compounds **5**–**8** in MeCN solution.

The absorption and emission in the visible region for **6**–**8** are probably due to a strong intramolecular charge transfer between the electron-rich diazepine and electron-poor dibenzothiophene-5,5-dioxide regions. This postulation is strengthened by solvatochromism observed as a blue shift in emission of up to 26 nm when moving from highly polar acetonitrile (ε_r = 37.5) to less polar chloroform (ε_r = 4.81, Figure S1 and Table S1). There is a substantial difference in color between the ketone products **6** and **7** (orange) and aldehyde product **8** (yellow).

The molecular structures of **5** (in three different crystal forms) and **6** were determined by single-crystal X-ray diffraction (see Supporting Information) and, in good agreement, calculated using the density functional theory (DFT, B3LYP/6-31G*). Both methods show molecule **5** adopting a twisted conformation of the dibenzothiophene system, in order to widen the short contacts N···N and N···O

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J. Org. Chem. XXXX, XXX, XXX−XXX

between adjacent nitro groups (Table 1), whereas in **6** the dibenzothiophene unit is practically planar, N(2) and N(3) are

Table 1. Experimental and Calculated Torsion Angles (Deg) and Interatomic Distances (Å)[a]

molecule	5	6	9
C5−C6−C7−C8/DFT	18.2	0	16.3
X-ray	18.0−23.5	1.2	
C1−C6−C7−C12/DFT	13.1	0	8.7
X-ray	12.0−14.4	0.7	
N2···N3/DFT	2.997	2.411	2.774
X-ray	2.901(3)−3.001(2)	2.425(2)	
N2···O5/DFT	2.681		
X-ray	2.587(7)−2.717(2)		
C6−C7/DFT	1.490	1.474	
X-ray	1.486(2)−1.494(4)	1.472(2)	

[a]For atom numbering, see Schemes 1 and 2.

coplanar with it, and their (postcyclization) separation is much shorter than in **5**, with the C6−C7 bond also shortening slightly. The 1,3-diazepine ring of **6** adopts a half-chair conformation with the N2−C15−N3 fragment inclined to the dibenzothiophene plane by 51.5(1)° (cf. calculated 34.6°). The accurate prediction of structures **5** and **6** by DFT analysis encouraged us to perform it for **9**, whose single crystals could not be obtained. The predicted structure is intermediate between those of **5** and **6** (Figure S5, Table 1).

Molecular orbital distributions for **5** and **6** (Figure 2) show a major contribution to the LUMO of **5** from the nitro groups,

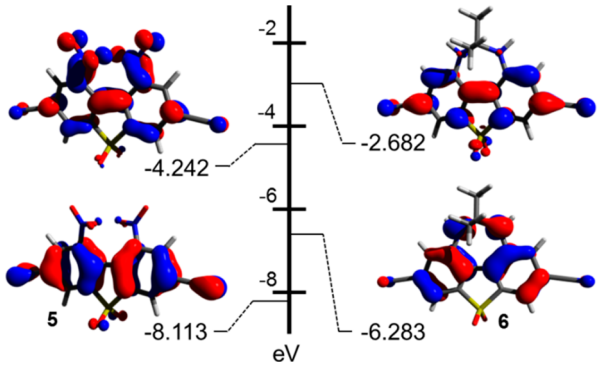

Figure 2. HOMO (lower) and LUMO (upper) contours for **5** and **6** and their calculated energies.

the nitrogen atoms of which subsequently become HOMO contributors upon reduction and cyclization to **6**. The results of identical calculations for **9** are shown in Figure S6.

An interesting feature of the diazepine precursor compound **5** is its ability to accept two electrons as shown in cyclic voltammetry (CV) experiments. The voltammogram in Figure 3 shows two, sequential, single-electron reductions at half-wave potentials of −0.15 and −0.45 V. Both processes are cleanly reversible, displaying a linear dependence between peak current and the square root of the scan rate (Figures S8 and S9) and peak separations close to the 59 mV expected for a one-electron wave. The data are summarized in Table S4 alongside a more detailed discussion of the properties of **5** in comparison with some related fluorenone-based acceptors.[56]

In conclusion, an efficient synthetic route has been established to an unusual highly functionalized fused-ring

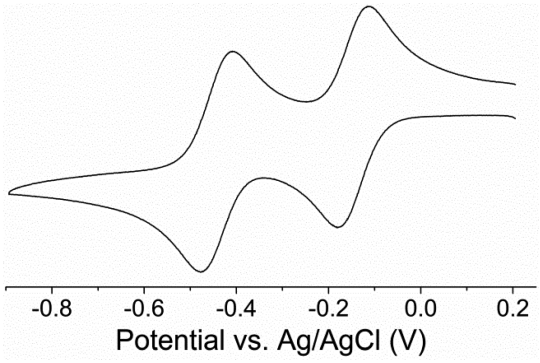

Figure 3. Cyclic voltammetry of **5**.

2,3-dihydro-1,3-diazepine system from the key dinitro compound **5** based on a one-pot reduction followed by reaction with aldehyde or ketone functionality. A comparison with 2,2′-dinitrobiphenyl shows that the structurally enforced proximity of the two amino groups in **9** is required for diazepine formation. There is a scope to exploit this chemistry in the synthesis of other interesting products. For example, the close proximity of the nitro groups in **5** suggests that ring closure to benzo[*c*]cinnoline-type scaffolds may also be feasible using alternative reaction conditions,[57−59] while other suitably nitrated carbo- and heterocycles such as fluorenes or carbazoles might behave similarly to **5**, providing further structural diversity for fused-ring 1,3-diazepines.

EXPERIMENTAL SECTION

General Methods. All reactions requiring an inert atmosphere were performed under a blanket of argon or nitrogen gas, which was dried though a column of phosphorus pentoxide. Anhydrous solvents were dried through an HPLC column on an innovative Technology Inc. solvent purification system. All reactants and reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. Column chromatography was carried out using silica gel 60, 40−60 μm mesh (Fluorochem). Analytical thin-layer chromatography was performed on precoated aluminum silica gel 60 F_{254} plates (Merck), which were approximately 2 cm × 6 cm in size, and visualized using ultraviolet light (254/365 nm). NMR spectra were recorded on the following specrtrometers: Bruker Avance-400 (^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz)), Varian Inova-500 (^{13}C NMR (125 MHz)), and Varian VNMRS-700 (^{1}H NMR (700 MHz), ^{13}C NMR (175 MHz)). Chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) using TMS or the residual solvent as an internal reference. NMR spectra were processed using MestreNova. Multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). Melting points were determined in open-ended capillaries using a Stuart Scientific SMP3 melting point apparatus at a ramping rate of 1 °C/min. They are recorded to the nearest 1 °C and are uncorrected. Mass spectrometry data were generated by Waters Ltd., U.K. (atmospheric solids analysis probe (ASAP) mass spectrometry). IR spectra were collected on a PerkinElmer Spectrum Two IR spectrometer. Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyzer. Cyclic voltammetry was recorded using a Princeton Applied Research VersaSTAT 3. A glassy carbon disk, Pt wire, and Ag/Ag$^+$ ($AgNO_3$ in acetonitrile) were used as the working, counter, and reference electrodes, respectively. Measurements were corrected to the ferrocene/ferrocenium redox couple as an internal standard and represented versus Ag/AgCl, which occurred at −0.45 V versus Fc/Fc$^+$ in these conditions. Acetonitrile was used as the solvent with an analyte molarity of ca. 10^{-4} M in the presence of 1 × 10^{-3} M (n-Bu_4N)(PF_6) as a supporting electrolyte. Solutions were degassed with Ar and experiments run under a blanket of Ar. UV−vis absorbance

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J. Org. Chem. XXXX, XXX, XXX−XXX

spectra were measured using a UV-1800 UV−vis spectrophotometer (Shimadzu) and UVProbe version 2.33 software. Emission spectra were recorded on an SPEX Fluoromax luminescence spectrometer using dM300 version 3.12 software. Density function theory (DFT) calculations were performed with ORCA v4.01[60] using the B3LYP hybrid functional and 6-31G* basis set.[61−63] Ground-state structural optimizations were performed prior to frontier orbital calculations.

*5,5-Dioxo-5H-dibenzo[b,d]thiophene-3,7-dicarboxylic Acid (**2**).*[50] A solution of dimethyl biphenyl-4,4′-dicarboxylate **1** (5.00 g, 19.0 mmol) in chlorosulfonic acid (20 mL) was heated at reflux for 3 h. The reaction mixture was cooled to room temperature and poured over ice to precipitate the product. The white precipitate was filtered and washed with water (50 mL), hexane (40 mL), and diethyl ether (40 mL). The white powder was recrystallized from acetone to afford **2** as a white crystalline solid (5.51 g, 95%): mp > 350 °C; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.43 (2H, d, J = 7.7 Hz, $H_{1/9}$), 8.38 (2H, d, J = 0.9 Hz, $H_{4/6}$), 8.36 (2H, dd, J = 8.0, 1.5 Hz, $H_{2/8}$).

*1,9-Dinitro-5,5-dioxo-5H-dibenzo[b,d]thiophene-3,7-dicarboxylic Acid (**3**).* A 1 L two-neck round-bottom flask equipped with a water-cooled reflux condenser and a pressure equalizing dropping funnel was charged with **2** (18.0 g, 59.2 mmol) and 95% sulfuric acid (d = 1.83, 165 mL) and placed in an ice batch. Fuming 90% nitric acid (d = 1.50, 250 mL) was added cautiously using to the stirred solution through the dropping funnel, while maintaining the temperature between 5−10 °C. The ice bath was swapped for a heating block, which was then slowly heated to 130 °C for 48 h. To minimize corrosive vapors escaping the reaction vessel, the top of the reflux condenser was connected by PVC tubing to an empty 500 mL Dreschel bottle (to avoid the risk of suck back into the reaction vessel), which in turn was connected by another length of PVC tubing, the end of which was submerged approximately 2 cm below the surface of 400 mL of water in a 1 L beaker. After heating, the mixture was allowed to cool and then was poured over ice. The white precipitate that formed was filtered and washed with water (60 mL) and then hexane (40 mL). The crude product was recrystallized from acetic acid to afford **3** as a white crystalline solid (17.1 g, 73%): mp > 350 °C; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.89 (2H, d, J = 1.5 Hz, $H_{2/8}$), 8.71 (2H, d, J = 1.5 Hz, $H_{4/6}$); ^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 163.6, 146.3, 141.0, 137.0, 131.1, 127.1, 123.9; IR (ν_{max}/cm^{-1}) 3095 (w), 2523 (br), 1707 (s, C═O), 1543 and 1359 (s, NO_2), 1326 and 1146 (s, SO_2), 1279 (s), 1185 (s), 1172 (s), 744 (s); MS (ASAP) m/z 395.0 [M + H]$^+$; HRMS (ASAP) m/z [M + H]$^+$ calcd for $C_{14}H_7N_2O_{10}S$ 394.9816, found 394.9811.

*1,9-Dinitro-5,5-dioxo-5H-dibenzo[b,d]thiophene-3,7-dicarboxamide (**4**).* A few drops of DMF were added to a suspension of **3** (15.0 g, 38.0 mmol) in thionyl chloride (380 mL), which was then heated to reflux for 3 h to form a yellow solution. After the mixture was cooled to room temperature, the excess thionyl chloride was removed under reduced pressure to afford a pale yellow solid (16.4 g, 38.0 mmol). The yellow solid was then suspended in water (20 mL) with stirring before a 35% aqueous ammonia solution (d = 0.88, 200 mL) was very carefully added dropwise (CAUTION! gas evolution). The reaction mixture was left to stir at room temperature for 2.5 h and then poured over ice to produce a brown precipitate, which was filtered off and washed with diethyl ether (50 mL) and then hexane (50 mL) to yield **4** as a pale brown solid (12.7 g, 86%). The compound was used without further purification: mp 230 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.96 (2H, d, J = 1.0 Hz, $H_{2/8}$), 8.81 (2H, d, J = 1.0 Hz, $H_{4/6}$), 8.61 (2H, s, NH), 8.12 (2H, s, NH); ^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 163.3, 146.2, 140.7, 139.6, 129.9, 125.4, 122.9; IR (ν_{max}/cm^{-1}) 3083 (br), 2924 (w), 1693 (s, C═O), 1616 (m, amide—H), 1541 and 1352 (s, NO_2), 1314 and 1145 (s, SO_2), 1386 (m), 1192 (m); MS (ASAP) m/z 393.0 [M + H]$^+$; HRMS (ASAP) m/z [M + H]$^+$ calcd for $C_{14}H_9N_4O_8S$ 393.0136, found 393.0135.

*3,7-Dicyano-1,9-dinitro-5,5-dioxo-5H-dibenzo[b,d]thiophene (**5**).* A solution of **4** (1.60 g, 4.08 mmol) in phosphorus oxychloride (40 mL) was heated to reflux for 3 h. The resulting dark orange solution was cooled to room temperature and quenched slowly with warm water. The orange precipitate was filtered and washed with water (50 mL) and hexane (30 mL). The crude product was recrystallized from acetonitrile and water to afford **5** as pale yellow crystals (1.30 g, 90%): mp 250 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 9.08 (2H, d, J = 1.5 Hz, $H_{2/8}$), 9.02 (2H, d, J = 1.5 Hz, $H_{4/6}$); ^{13}C NMR (101 MHz, acetone-d_6, ppm) δ 147.9, 142.8, 135.4, 131.6, 125.5, 119.0, 115.8; IR (ν_{max}/cm^{-1}) 3074 (w), 2242 (C≡N, w), 1547 and 1352 (NO_2, s), 1495 (m), 1330 and 1161 (SO_2, s), 1227 (m), 1188 (m), 778 (m), 737 (s), 694 (s), 575 (m), 544 (s), 467 (s). Elemental Anal. Calcd for $C_{14}H_4N_4O_6S$: C, 47.20; H, 1.13; N, 15.73. Found: C, 46.84; H, 1.12; N, 15.70. Despite repeated attempts using a range of techniques, this molecule was not observed by mass spectrometry. Single crystals for X-ray analysis were grown from both ethyl acetate/hexane and THF/MeOH/H_2O solutions.

*N,N′-Isopropylidene-1,9-diamino-3,7-dicyano-5,5-dioxo-5H-dibenzo[b,d]thiophene (**6**).* To a stirred solution of $SnCl_2$·$2H_2O$ (3.00 g, 13.4 mmol) in a mixture of methanol (8.50 mL) and aqueous HCl (2 M, 8.5 mL) were added acetone (1.00 mL, 13.6 mmol, 16 equiv) and **5** (0.30 g, 0.84 mmol) sequentially. The mixture was then heated to 85 °C for 2.5 h. The mixture was cooled to room temperature and poured into aqueous HCl (2 M, 34 mL). An orange precipitate immediately formed, which was filtered and washed with hexane (30 mL). It was then purified by silica column chromatography (eluent 30:70 hexane/ethyl acetate (v/v)) to afford **6** as an orange powder (128 mg, 45%): mp 350 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 7.64 (2H, d, J = 1.3 Hz, $H_{4/6}$), 7.44 (2H, d, J = 1.3 Hz, $H_{2/8}$), 6.98 (2H, s, NH), 1.63 (6H, s, CH_3); ^{13}C NMR (101 MHz, acetone-d_6, ppm) δ 146.1, 140.2, 126.9, 119.1, 118.0, 114.6, 114.3, 67.2, 28.4; IR (ν_{max}/cm^{-1}) 3331 (N—H, m), 2917 (w), 2233 (C≡N, m), 1740 (m), 1606 (m), 1526 (m), 1457 (m), 1367 (m), 1308 and 1150 (SO_2, s), 1278 (m), 1028 (m), 876 (m), 713 (m), 624 (m), 545(s); MS (ASAP) m/z 337.1 [M + H]$^+$; HRMS (ASAP) m/z [M + H]$^+$ calcd for $C_{17}H_{13}N_4O_2S$ 337.0754, found 337.0753.

*N,N′-Cyclohexylidene-1,9-diamino-3,7-dicyano-5,5-dioxo-5H-dibenzo[b,d]thiophene (**7**).* To a stirred solution of $SnCl_2$·$2H_2O$ (5.07 g, 22.5 mmol) in a mixture of methanol (14 mL) and aqueous HCl (2 M, 14 mL) were added cyclohexanone (0.73 mL, 7.0 mmol) and **5** (0.50 g, 1.40 mmol). The mixture was then heated to 85 °C for 2.5 h. The mixture was cooled to room temperature and poured into aqueous HCl (2 M, 56 mL). An orange precipitate immediately formed, which was filtered and washed with hexane (30 mL). It was then purified by silica column chromatography (eluent 40:60 hexane/ethyl acetate (v/v)) to afford **7** as small orange crystals (230 mg, 44%): mp 300 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 7.64 (2H, d, J = 1.3 Hz, $H_{4/6}$), 7.59 (2H, d, J = 1.3 Hz, $H_{2/8}$), 6.84 (2H s, NH), 1.92−1.84 (4H, m, CH_2), 1.69−1.49 (6H, m, CH_2); ^{13}C NMR (101 MHz, acetone-d_6, ppm) δ 145.5, 140.1, 127.2, 119.6, 118.0, 114.7, 114.3, 68.8, 36.1, 25.8, 22.4; IR (ν_{max}/cm^{-1}) 3401 (m), 3356 (m), 3321 (N—H, m), 3076 (w), 2941 (w), 2241 (C≡N, m), 1606 (m), 1517 (s), 1305 and 1150 (SO2, s) 852 (m), 708 (m), 620 (m); MS (ASAP) m/z 377.1 [M + H]$^+$; HRMS (ASAP) m/z [M + H]$^+$ calcd for $C_{20}H_{17}N_4O_2S$ 377.1067, found 377.1067.

*N,N′-(4-tert-Butylbenzylidene)-1,9-diamino-3,7-dicyano-5,5-dioxo-5H-dibenzo[b,d]thiophene (**8**).* To a stirred solution of $SnCl_2$·$2H_2O$ (2.02 g, 8.99 mmol) in a mixture of methanol (6 mL) and aqueous HCl (2 M, 6 mL) were added 4-*tert*-butylbenzaldehyde (0.50 mL, 2.81 mmol) and **5** (0.20 g, 0.56 mmol). The mixture was then heated to 85 °C for 2.5 h. The mixture was cooled to room temperature and poured into aqueous HCl (2 M, 25 mL). The organics were then extracted into ethyl acetate (3 × 15 mL) and washed with water (2 × 25 mL). The organic fractions were dried over magnesium sulfate, and ethyl acetate was removed under a vacuum to afford an oil. The oil was dissolved in dichloromethane (30 mL), and hexane (20 mL) was added. The solvent was reduced in volume (ca. 10 mL) to precipitate the crude product as a yellow powder. It was then purified by silica column chromatography (eluent 70:30 hexane/ethyl acetate (v/v)) to afford **8** as a yellow crystalline powder (92 mg, 39%): mp 300 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 7.69 (2H, d, J = 1.4 Hz, $H_{4/6}$), 7.65 (2H, d, J = 1.4 Hz, $H_{2/8}$), 7.58−7.48 (4H, m, $H^{4\text{-}t\text{-}BuC_6H_4}$), 7.17 (2H, s, NH), 5.34 (1H, s, CH), 1.36 (9H, s, CH_3); ^{13}C NMR (101 MHz, acetone-d_6,

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J. Org. Chem. XXXX, XXX, XXX−XXX

ppm) δ 153.2, 148.5, 140.7, 136.7, 128.3, 126.9, 126.4, 118.9, 118.0, 115.2, 113.8, 71.2, 35.3, 31.6; IR (ν_{max}/cm^{-1}) 3355 (N—H, w), 3063 (w), 2956 (w), 2233 (C≡N, m), 1605 (m), 1505 (s), 1468 (s), 1305 and 1145 (SO_2, s), 1268 (m), 1202 (m), 886 (m), 836 (m), 707 (m), 621 (m); MS (ASAP) m/z 441.1 $[M + H]^+$; HRMS (ASAP) m/z $[M + H]^+$ calcd for $C_{25}H_{21}N_4O_2S$ 441.1380, found 441.1374.

*1,9-Diamino-3,7-dicyano-5,5-dioxo-5H-dibenzo[b,d]thiophene (**9**).* To a stirred solution of $SnCl_2{\cdot}2H_2O$ (5.07 g, 22.5 mmol) in a mixture of ethanol (14 mL) and aqueous HCl (2 M, 14 mL) was added **5** (0.50 g, 1.40 mmol). The mixture was heated to 85 °C for 2.5 h, then cooled to room temperature, and poured into aqueous HCl (2 M, 56 mL). An orange precipitate immediately formed, which was filtered and washed with hexane (30 mL). The product was purified by silica column chromatography (eluent 30:70 hexane/ethyl acetate (v/v), gradually increased polarity to 100% ethyl acetate) to afford **9** as a light brown powder (60 mg, 14%): mp 300 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.79 (2H, d, J = 1.5 Hz, $H_{4/6}$), 7.52 (2H, d, J = 1.5 Hz, $H_{2/8}$), 6.60 (4H, s, NH_2); ^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 145.0, 139.1, 126.5, 118.1, 117.6, 112.9, 112.6; IR (ν_{max}/cm^{-1}) 3451 and 3360 (N—H, m), 3243 (w), 3070 (w), 2226 (C≡N, s), 1632 and 1598 (NH_2, s), 1543 (m), 1467 (m), 1430 (m), 1346 (m), 1299 and 1143 (SO_2, s), 1253 (m), 1194 (m), 881 (m), 617 (m); MS (ASAP) m/z 297.0 $[M + H]^+$; HRMS (ASAP) m/z $[M + H]^+$ calcd for $C_{14}H_9N_4O_2S$ 297.0441, found 297.0437.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02029.

^{1}H and ^{13}C NMR spectra for all new compounds, absorption and emission spectra, computational details for **5**, **6**, and **9**, computational results for **9**, electrochemical properties of **1**, and further crystallographic details (PDF)

Crystal data for **5**, **5**·1/2 THF, and **6** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: i.a.wright@lboro.ac.uk.

*E-mail: m.r.bryce@durham.ac.uk.

ORCID

Iain A. Wright: 0000-0002-0142-2809

Andrei S. Batsanov: 0000-0002-4912-0981

Martin R. Bryce: 0000-0003-2097-7823

Notes

The authors declare no competing financial interest.

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