Supplementary Material

Flash vacuum pyrolysis of 2-acetyl-3-azido[1]benzothiophene

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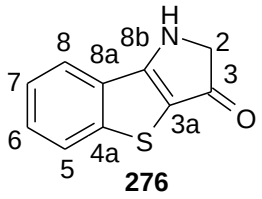
S1. Preparation of 2-Acetyl-3-amino[1]benzothiophene (**10**)

A solution of pentane-2,4-dione (0.60 g, 6 mmol) in ethanol (2 cm^3) was added dropwise with stirring over 10 min to a cooled solution of sodium ethoxide [from sodium (0.15 g, 6.5 mmol) and ethanol (8 cm^3)], and stirred for a further 20 min with cooling. Crushed 3-chloro-1,2-benzisothiazole (1.00 g, 5.97 mmol) was then added at room temperature, stirred for 30 min, then heated under reflux for 16 h. The mixture was cooled to room temperature and added to ice (40 cm^3). The resulting precipitate was collected and washed with water and ethanol to yield 2-acetyl-3-amino[1]benzothiophene (**10**) (900 mg, 80%); mp 142–144 °C (lit.,[1] 145.5–147 °C); δ_H 2.42 (3H, s, CH_3), 6.77 (2H, br, NH_2), 7.34 (1H, m, Ar-H), 7.49 (1H, m, Ar-H) and 7.65 – 7.72 (2H, m, 2 × Ar-H); δ_C 28.93 (CH_3), 108.6 (quat), 121.6, 123.3, 124.0, 128.8, 131.0 (quat), 139.7 (quat), 148.6 (quat) and 193.1 (quat); *m/z* 191 (M^+, 96 %), 177 (28), 176 (100), 148 (65), 121 (69) and 77 (37). The crystallographic data has been deposited at the Cambridge Crystallographic Data Centre and assigned the code number CCDC1416874.

S2. NMR analysis of 1,2-dihydro-3*H*-[1]benzothieno[3,2-*b*]pyrrol-3-one (9K)



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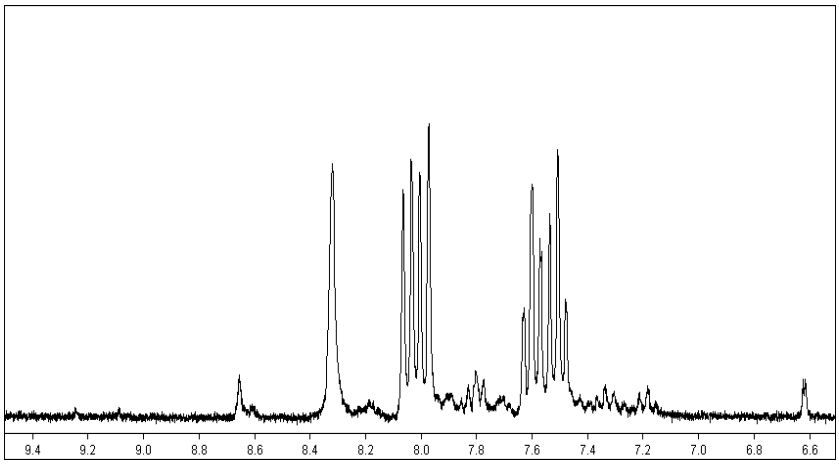


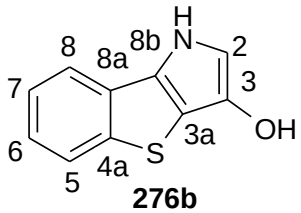
Figure 1. ^{1}H NMR spectrum of 1,2-dihydro-3*H*-[1]benzothieno[3,2-*b*]pyrrol-3-one (**9K**) from the 600 °C FVP of 2-acetyl-3-azido[1]benzothiophene (**11**). Minor peaks are due to the enol form **9E**.

For the keto tautomer, a NOESY experiment showed an interaction between the NH peak and the aromatic signal at δ 8.05, indicating this signal to be from H(8). A COSY experiment then indicated the identity of the remaining aromatic signals around the benzene ring, whilst a HSQC experiment showing one bond hydrogen to carbon coupling allowed identification of the four non-quaternary carbons from the aromatic ring. A HMBC experiment, showing long range hydrogen to carbon bonding, allowed full identification of the remaining quaternary carbons. H(6) and H(8) were shown to give strong coupling to the carbon at δ 148.0, showing it to be C(4a), whilst H(5) and H(7) were shown to give a strong coupling to the carbon at δ 126.0 showing it to be C(8a). H(8) and H(2) gave coupling to the carbon at δ 171.4, indicating it to be C(8b). Of the two remaining unassigned quaternaries at δ 109.5 and δ 190.4, the chemical shift of δ 190.4 indicates it to be the carbonyl at C(3), meaning that δ 109.5 is C(3a). The full analysis is listed in Table S1.

Table S1. NMR characterisation of the keto tautomer 1,2-dihydro-3*H*[1]benzothieno[3,2-*b*]pyrrol-3-one (**9K**)

Position	δ_H	δ_C
2	4.32	60.1
3		190.4
3a		109.5
4a		148.0
5	7.98	125.2
6	7.60	129.5
7	7.51	125.0
8	8.05	123.6
8a		126.0
8b		171.4

S3. NMR analysis of 3-hydroxy[1]benzothieno[3,2-*b*]pyrrole (9E)



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Similarly for the enol tautomer, **9E**, NOESY, COSY and HSQC experiments were used to identify the four CHs around the aromatic ring. A HMBC experiment showed coupling from H(6) and H(8) to the carbon at δ 140.7 indicating this to be C(4a), whilst H(5) and H(7) showed coupling to the carbon at δ 127.8 indicating this to be C(8a). H(2) and H(8) showed coupling to the carbon at δ 129.86 indicating this to be C(8b). The remaining two peaks at δ 109.89 and δ 137.1 were assigned by comparison with those previously observed for hydroxypyrroles *viz* C(3) at *ca.* δ 139-151 and C(3a) at *ca*. δ 95-103.[2] The full analysis is listed in Table S2.

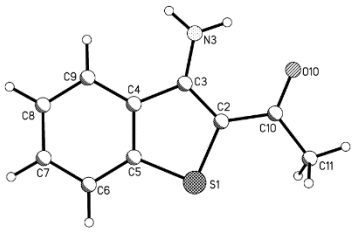
Table S2. NMR characterisation of the enol tautomer 3-hydroxy-1*H*-[1]benzothieno[3,2-*b*]pyrrole (**9E**)

Position	δ_H	δ_C
2	6.62	107.1
3		137.1
3a		109.9
4a		140.7
5	7.81	124.2
6	7.18	122.4
7	7.34	124.1
8	7.79	118.5
8a		127.8
8b		129.9

S4. X-Ray crystallography

For reference, bond lengths and angles of 2-acetyl-3-aminobenzo[*b*]thiophene (**10**) (Table S3) and 2-acetyl-3-azido-1-benzothiophene (**11**) (Table S4) are reproduced below. The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and assigned the code numbers CCDC1416874 and CCDC1408196, respectively.

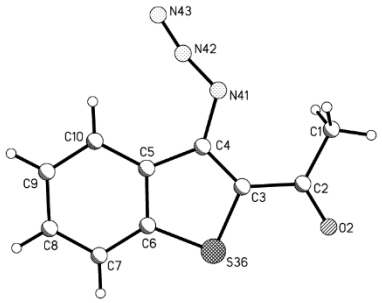
Table 3. Bond lengths [Å] and angles (deg) for the two molecules of 2-acetyl-3-amino[1]benzothiophene **(10)**



Bond lengths/Å	Bond angles/°
	C5 . S1 . C2 . 91.03(7)
S1 . C5 . 1.7353(15)	C10 . C2 . C3 . 125.51(13)
S1 . C2 . 1.7548(14)	C10 . C2 . S1 . 121.98(11)
C2 . C10 . 1.434(2)	C3 . C2 . S1 . 112.52(11)
C2 . C3 . 1.387(2)	C4 . C3 . N3 . 123.17(14)
C3 . C4 . 1.445(2)	C4 . C3 . C2 . 112.16(13)
C3 . N3 . 1.351(2)	N3 . C3 . C2 . 124.66(14)
C4 . C9 . 1.399(2)	C9 . C4 . C5 . 119.66(14)
C4 . C5 . 1.407(2)	C9 . C4 . C3 . 128.56(14)
C5 . C6 . 1.398(2)	C5 . C4 . C3 . 111.77(13)
C6 . C7 . 1.382(3)	C6 . C5 . S1 . 126.20(13)
C7 . C8 . 1.398(3)	C6 . C5 . C4 . 121.27(15)
C8 . C9 . 1.383(2)	S1 . C5 . C4 . 112.53(11)
C10 . C11 . 1.504(2)	C7 . C6 . C5 . 117.98(16)
C10 . O10 . 1.242(2)	C8 . C7 . C6 . 121.29(15)
	C9 . C8 . C7 . 120.85(16)
S11 . C15 . 1.7300(16)	C8 . C9 . C4 . 118.93(15)
S11 . C12 . 1.7581(15)	C11 . C10 . O10 . 120.08(15)
C12 . C20 . 1.430(2)	C11 . C10 . C2 . 119.26(14)
C12 . C13 . 1.390(2)	O10 . C10 . C2 . 120.65(14)
C13 . C14 . 1.447(2)	
C13 . N13 . 1.346(2)	C15 . S11 . C12 . 91.10(7)
C14 . C19 . 1.399(2)	C20 . C12 . C13 . 125.96(14)
C14 . C15 . 1.406(2)	C20 . C12 . S11 . 121.69(12)
C15 . C16 . 1.398(2)	C13 . C12 . S11 . 112.32(11)
C16 . C17 . 1.380(3)	C14 . C13 . N13 . 123.13(14)
C17 . C18 . 1.397(3)	C14 . C13 . C12 . 112.08(13)
C18 . C19 . 1.384(2)	N13 . C13 . C12 . 124.76(14)

C20 . C21 . 1.505(3)	C19 . C14 . C15 . 119.34(14)
C20 . O20 . 1.247(2)	C19 . C14 . C13 . 128.91(14)
	C15 . C14 . C13 . 111.73(14)
	C16 . C15 . S11 . 126.28(13)
	C16 . C15 . C14 . 120.99(15)
	S11 . C15 . C14 . 112.73(11)
	C17 . C16 . C15 . 118.45(15)
	C18 . C17 . C16 . 121.36(15)
	C19 . C18 . C17 . 120.19(16)
	C18 . C19 . C14 . 119.65(15)
	C21 . C20 . O20 . 120.45(15)
	C21 . C20 . C12 . 118.45(15)
	O20 . C20 . C12 . 121.09(16)

Table S4. Bond lengths [Å] and angles (deg) for the two molecules of 2-acetyl-3-azido[1]benzothiophene (**11**)



Bond lengths/Å	Bond angles/°
C1 . C2 . 1.4958(18)	C1 . C2 . O2 . 120.78(11)
C2 . O2 . 1.2278(15)	C1 . C2 . C3 . 120.59(10)
C2 . C3 . 1.4707(16)	O2 . C2 . C3 . 118.62(12)
C3 . S36 . 1.7399(12)	C2 . C3 . S36 . 116.04(9)
C3 . C4 . 1.3761(15)	C2 . C3 . C4 . 131.78(11)
S36 . C6 . 1.7281(12)	S36 . C3 . C4 . 112.17(8)
C4 . N41 . 1.4078(14)	C3 . S36 . C6 . 91.63(5)
C4 . C5 . 1.4456(15)	C3 . C4 . N41 . 120.17(10)
N41 . N42 . 1.2425(13)	C3 . C4 . C5 . 113.08(10)
N42 . N43 . 1.1284(14)	N41 . C4 . C5 . 126.69(10)
C5 . C6 . 1.4122(15)	C4 . N41 . N42 . 119.26(10)
C5 . C10 . 1.4045(15)	N41 . N42 . N43 . 169.40(12)
C6 . C7 . 1.4003(16)	C4 . C5 . C6 . 110.80(10)
C7 . C8 . 1.3754(17)	C4 . C5 . C10 . 130.30(10)
C8 . C9 . 1.4020(18)	C6 . C5 . C10 . 118.89(10)
C9 . C10 . 1.3796(16)	C5 . C6 . S36 . 112.33(8)
	C5 . C6 . C7 . 121.48(11)

C101 . C102 . 1.4988(17)	S36 . C6 . C7 . 126.18(9)
C102 . O102 . 1.2220(15)	C6 . C7 . C8 . 118.33(11)
C102 . C103 . 1.4772(16)	C7 . C8 . C9 . 120.92(11)
C103 . S136 . 1.7412(11)	C8 . C9 . C10 . 121.15(11)
C103 . C104 . 1.3780(15)	C5 . C10 . C9 . 119.22(11)
S136 . C106 . 1.7274(12)	
C104 . N141 . 1.4060(14)	C101 . C102 . O102 . 121.36(11)
C104 . C105 . 1.4424(15)	C101 . C102 . C103 . 119.97(10)
N141 . N142 . 1.2397(14)	O102 . C102 . C103 . 118.66(11)
N142 . N143 . 1.1293(15)	C102 . C103 . S136 . 115.91(8)
C105 . C106 . 1.4139(15)	C102 . C103 . C104 . 131.88(10)
C105 . C110 . 1.4079(15)	S136 . C103 . C104 . 112.21(8)
C106 . C107 . 1.4006(15)	C103 . S136 . C106 . 91.42(5)
C107 . C108 . 1.3731(18)	C103 . C104 . N141 . 119.64(10)
C108 . C109 . 1.4011(17)	C103 . C104 . C105 . 113.15(9)
C109 . C110 . 1.3793(16)	N141 . C104 . C105 . 127.19(10)
	C104 . N141 . N142 . 119.69(10)
	N141 . N142 . N143 . 169.21(12)
	C104 . C105 . C106 . 110.63(10)
	C104 . C105 . C110 . 130.59(10)
	C106 . C105 . C110 . 118.77(10)
	C105 . C106 . S136 . 112.58(8)
	C105 . C106 . C107 . 121.49(11)
	S136 . C106 . C107 . 125.92(9)
	C106 . C107 . C108 . 118.29(11)
	C107 . C108 . C109 . 121.14(11)
	C108 . C109 . C110 . 121.09(11)
	C105 . C110 . C109 . 119.22(11)

S5. References

1. Carrington, D. E. M.; Clarke, K.; Scrowston, R. M. *J. Chem. Soc. (C)*, **1971**, 3903-3906.
2. McNab, H.; Monahan, L. C. *J. Chem. Soc., Perkin Trans 2*, **1991**, 1999-2002

