Synthesis of Novel 2,3-Dihydro-8*H*-thieno[2,3-*d*]azepines and 1,2,3,4-Tetrahydro-1*H*-3-benzazepines *via* Photolyses of 6-Azido-2,3-dihydrobenzo[*b*]thiophene and 6-Azido-1,2,3,4-tetrahydronaphthalene[1]

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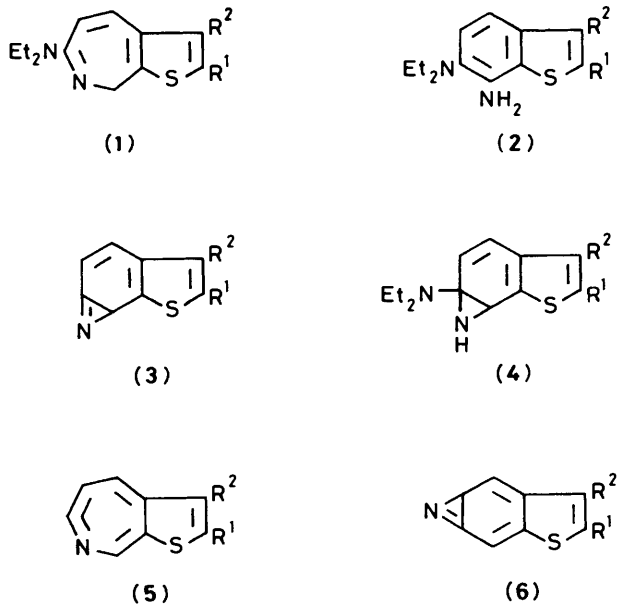
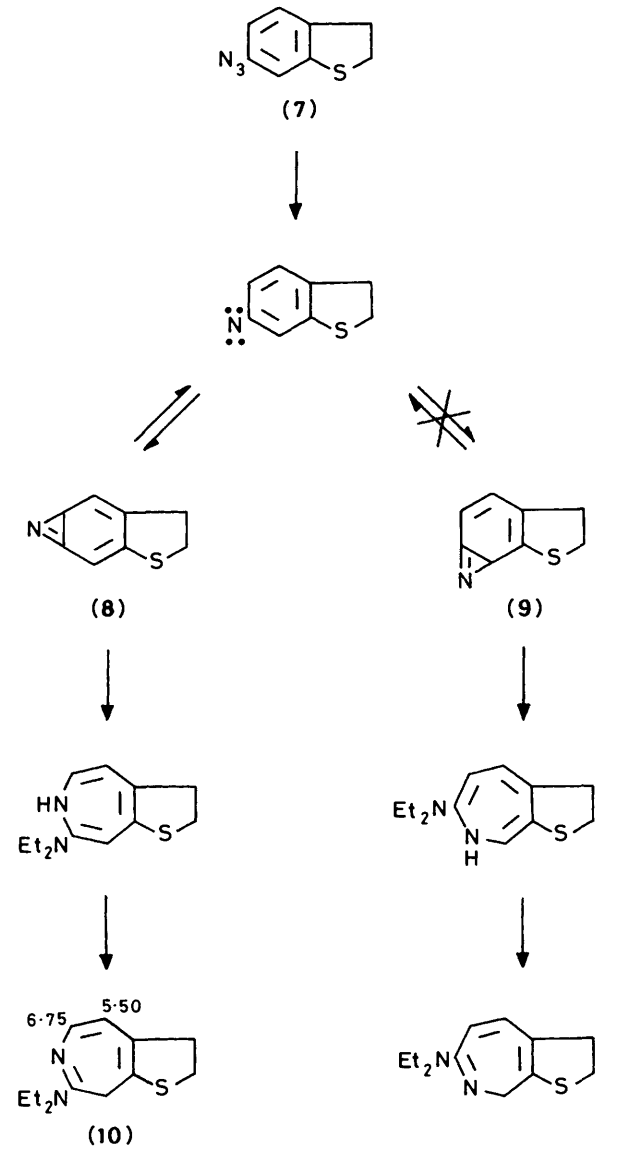
Reduction of 6-amino-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide with DIBAL-H gave 6-amino-2,3-dihydrobenzo[*b*]thiophene which was converted by standard procedures into 6-azido-2,3-dihydrobenzo[*b*]thiophene (**7**). Photolysis of this azide in an excess of diethylamine gave 7-diethylamino-2,3-dihydro-8*H*-thieno[2,3-*d*]azepine (**10**) whose structure was confirmed by ^{1}H n.m.r. spectroscopic studies and by conversion through successive bromination and elimination of hydrogen bromide from the intermediate into 7-diethylamino-8*H*-thieno[2,3-*d*]azepine (**13**), which was shown to be different from 6-diethylamino-8*H*-thieno[2,3-*c*]azepine (**12**), prepared by debromination of its 2,3-dibromo derivative (**11**). By contrast with the behaviour of azide (**7**), irradiation of 6-azido-1,2,3,4-tetrahydronaphthalene (**14**) in THF containing diethylamine or morpholine gave a mixture of the two possible azepines, (**17**) and (**19**) or (**18**) and (**20**), respectively, with (**19**) and (**20**) being the major isomers.

Whereas 4-[2] and 7-azidobenzo[*b*]thiophenes[3] (termed 'α-azides'; naphthalene nomenclature) give mixtures of 4(or 7)-aminobenzo[*b*]thiophenes and 4,4′(or 7,7′)-azobenzo[*b*]thiophenes (triplet-nitrene-derived products), respectively, when irradiated in an excess of diethylamine, 5-azidobenzo[*b*]thiophenes ('β-azides') give the corresponding 4-amino-5-diethylaminobenzo[*b*]thiophene (singlet-nitrene-derived products).[2] By contrast, photolysis of 6-azidobenzo[*b*]thiophenes ('β-azides') in an excess of diethylamine gives the corresponding 6-diethylamino-8*H*-thieno[2,3-*c*]azepine (**1**) or 7-amino-6-diethylaminobenzo[*b*]thiophene (**2**) or a mixture of both (singlet-nitrene-derived products), depending on the substituents, R^1 and R^2.[4] 6-Azidobenzo[*b*]thiophenes became the first class of bicyclic aromatic azide to undergo ring-expansion.[4,5] Other bicyclic heterocycles (*e.g.* 6-azidobenzothiazoles) behave similarly.[3,5] The products, (**1**) and (**2**), formed from 6-azidobenzo[*b*]thiophenes are formed probably *via* the intermediacy of 6-benzo[*b*]thienyl nitrenes, azirines (**3**), and aziridines (**4**), although the involvement of didehydrothienoazepines (**5**) cannot be ruled out.[6] Localisation of π-electrons ('bond fixation') in the 6.7-bonds of the 6-azidobenzo[*b*]thiophenes, leading to azirines (**3**), appears to be an important controlling factor in our reactions since products arising from the isomeric azirines (**6**) have not been detected to date, which may be due to a loss of aromaticity in the thiophene ring of these intermediates (**6**) [this is true also of compounds (**5**)]. It seemed important, therefore, to study the photolysis reactions of 6-azido-2,3-dihydrobenzo[*b*]thiophenes.

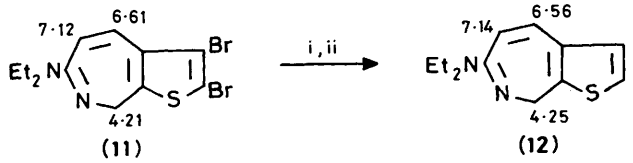
Oxidation of commercially available benzo[*b*]thiophene to its 1,1-dioxide followed by nitration, which gives a high yield of 6-nitrobenzo[*b*]thiophene 1,1-dioxide, conveniently introduces nitrogen functionality into the 6-position of this ring system.[4,7-9] 6-Nitrobenzo[*b*]thiophene 1,1-dioxide can be reduced to 6-aminobenzo[*b*]thiophene 1,1-dioxide or its 2,3-dihydro derivative but our previous attempts[4,7] to reduce the sulphone moiety in these systems back to the sulphide oxidation level have failed. For example, in our hands use of lithium aluminium hydride[10] gave complex mixtures (t.l.c.) from which 6-amino-2,3-dihydrobenzo[*b*]thiophene could not be isolated. We have discovered, however, that 6-amino-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide[7] is reduced in high yield (73%) to 6-amino-2,3-dihydrobenzo[*b*]thiophene with di-isobutylaluminium hydride (DIBAL-H)[11] (purchased from Aldrich as a 25% w/w solution in toluene). This amine was converted by standard procedures (*e.g.*, see ref. 12) into 6-azido-2,3-dihydrobenzo[*b*]thiophene (**7**), which could be kept at −20 °C for up to 12 months.



Photolysis of this azide (**7**) in a mixture of diethylamine and tetrahydrofuran (THF) (which stabilises singlet nitrenes[5]) for *ca.* 7 h under nitrogen gave, after chromatography of the product, starting material (10% recovery) and 7-diethylamino-2,3-dihydro-8*H*-thieno[2,3-*d*]azepine (**10**) (49% yield based on azide consumed) (Scheme 1). 6-Amino-2,3-dihydrobenzo[*b*]-thiophene was detected by ^{1}H n.m.r. spectroscopy and chromatography in the crude product. The conversion of azide (**7**) into thienoazepine (**10**) is the first example in our work of a



Scheme 1.

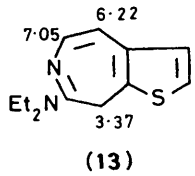


Scheme 2. *Reagents:* i, BuLi–Et_2O; ii, H_2O

5,6-bicyclic azide proceeding to ring-expand *via* an azirine of type (**8**) rather than type (**9**).

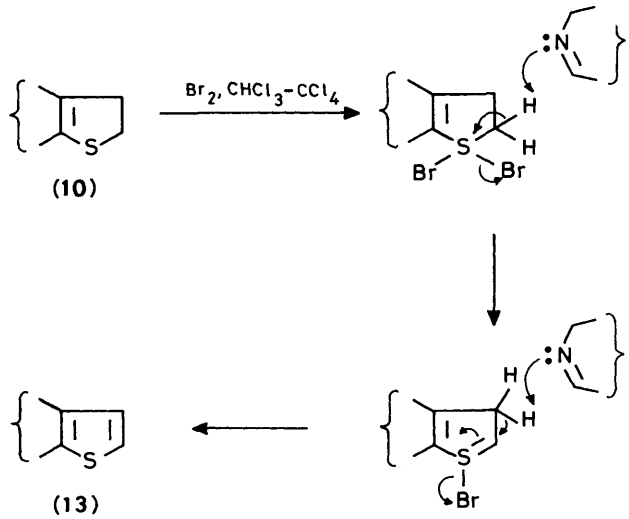
Previously we[4] assigned the structure of 8*H*-thieno[2,3-*c*]-azepines, *e.g.* (**11**) (Scheme 2), on the basis that the protons of a methylene group adjacent to an amidine C-atom resonate at higher field than those in one next to an amidine N-atom.[13] Further evidence for structure (**11**) was provided by addition of $Eu(fod)_3$* to the ^1H n.m.r. sample, which resulted in a considerable downfield shift of the methylene signal at δ 4.21 owing to complexation of the shift reagent between the ring and side-chain *N*-atoms, whilst the signal for the olefin proton (5-H) at δ 7.12 was shifted no more than that for the side-chain methylene protons. Structure (**10**) is assigned on the basis that the reverse is true, namely that the signal for the methylene group at position 8 is at a higher field (a multiplet is present at δ 3.40, which consists of this signal overlapping the quartet produced by the side-chain methylene protons) and addition of $Eu(fod)_3$ to the ^1H n.m.r. sample produces a small downfield shift of the signal for this methylene group but a considerable downfield shift of the signal for the olefinic proton (5-H), originally at δ 6.75.

To confirm structures (**10**) and (**11**) the former was treated with bromine in trichloromethane–tetrachloromethane at low temperatures, which gave a low yield (30% crude) of 7-diethylamino-8*H*-thieno[2,3-*d*]azepine (**13**), a solid, m.p. 56.5–57.5 °C, whilst the latter, compound (**11**), was debrominated by successive treatment with butyl-lithium and water, to give starting material (32% recovery) and 6-diethylamino-8*H*-thieno[2,3-*c*]azepine (**12**) (Scheme 2) (37% based on starting material consumed), as a pale yellow oil. Spectroscopic analysis of compounds (**12**) and (**13**) showed them to be isomeric (see, *e.g.*, the chemical shifts given with the formulae). A significant difference between the pairs of compounds (**10**) and (**13**) and (**11**) and (**12**) lies in the coupling constants for their olefinic protons, namely *J* 8.0 and 12.0 Hz, respectively.



Attempts to dehydrogenate the thienoazepine (**10**), to give compound (**13**), with palladium–charcoal, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, nickel peroxide, or manganese dioxide all failed. The successful conversion, (**10**) ⟶ (**13**), using elemental bromine may occur *via* bromination in the 2-position (*cf.* ref. 14) followed by base-catalysed elimination of hydrogen bromide, although the mechanism shown in Scheme 3 cannot be ignored.[15,16]

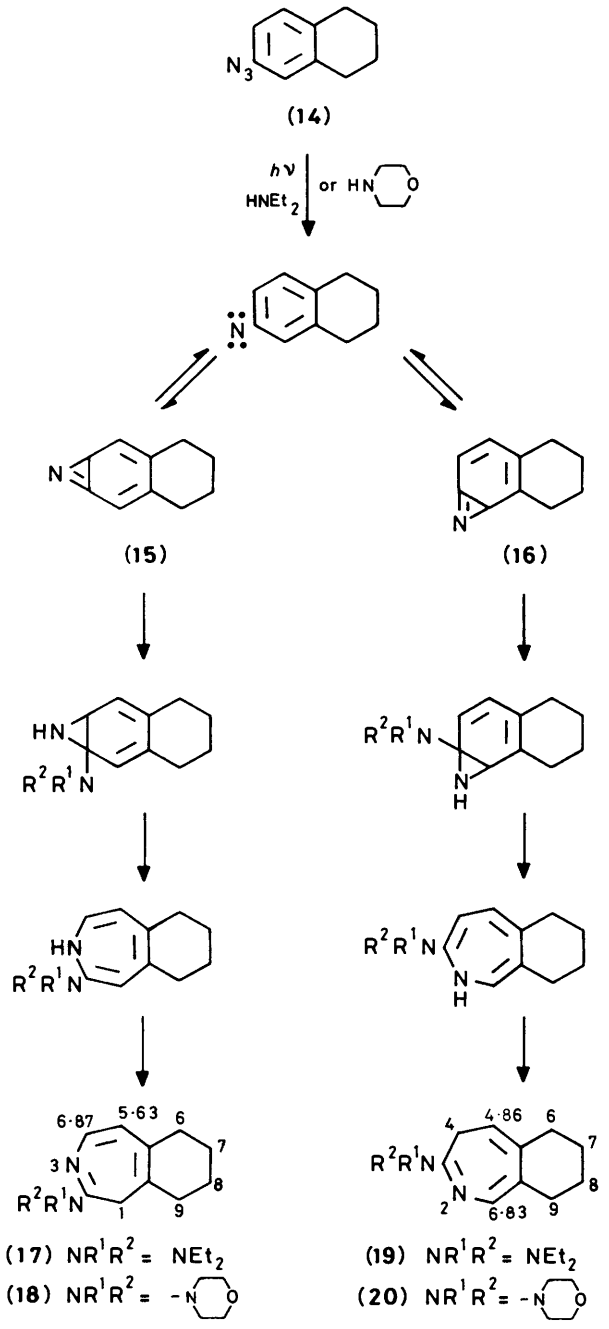
For comparison with the behaviour of 6-azido-2,3-dihydrobenzo[*b*]thiophene (**7**) on irradiation in THF in the presence of an excess of diethylamine we decided to investigate analogous



Scheme 3.

* Europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate).

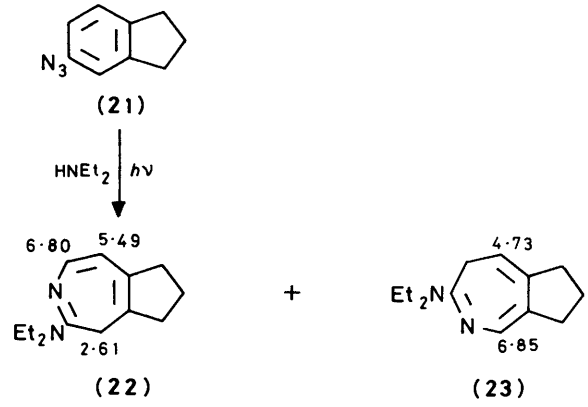
reactions of 6-azido-1,2,3,4-tetrahydronaphthalene (**14**). The starting material (**14**) was prepared by standard procedures from the corresponding amine, prepared in turn preferably through acetylation of 1,2,3,4-tetrahydronaphthalene[17] followed by a Schmidt reaction on the resulting 6-acetyl derivative and hydrolysis of the product, namely 6-acetamido-1,2,3,4-tetrahydronaphthalene. 6-Amino-1,2,3,4-tetrahydronaphthalene was prepared also, though less conveniently, by reduction of the corresponding 6-nitro compound. Nitration of 1,2,3,4-tetrahydronaphthalene under various reaction conditions gives a mixture of the 4- and 6-nitro isomers. For this nitration we preferred Schroeter's[18] conditions (nitration with nitrating mixture at 0 °C) despite a claim by Cumming and Howie[19] that reaction is incomplete at this temperature. We separated the two nitro isomers either by conventional chromatography on an alumina column or, more efficiently, by medium-pressure chromatography on alumina. However, chromatographic separations suffer from limitations of scale.



Scheme 4.

Irradiation of 6-azido-1,2,3,4-tetrahydronaphthalene (**14**) in THF in the presence of either diethylamine or morpholine gave in each case an inseparable mixture of azepines, (**17**) and (**19**), or (**18**) and (**20**) (Scheme 4), respectively, in the same ratio [isomers (**19**) and (**20**) were the major isomers] (by ^{1}H n.m.r. spectroscopy). We were able to assign these structures by recording the ^{1}H n.m.r. spectrum of the mixture and comparing the chemical shifts of the olefinic protons with literature data (CHN data for the mixtures of isomers also agreed with the assigned structures). In this case, therefore, both possible intermediate azepines, (**15**) and (**16**), are involved.

Thus, when Carde and Jones[20] irradiated 5-azidoindan (**21**) in neat diethylamine, they obtained a mixture (31% yield) of the isomeric aza-azulenes (**22**) and (**23**) (ratio 85:15 by ^{1}H n.m.r. spectroscopy) (Scheme 5). Addition of Eu(fod)$_3$ to a solution

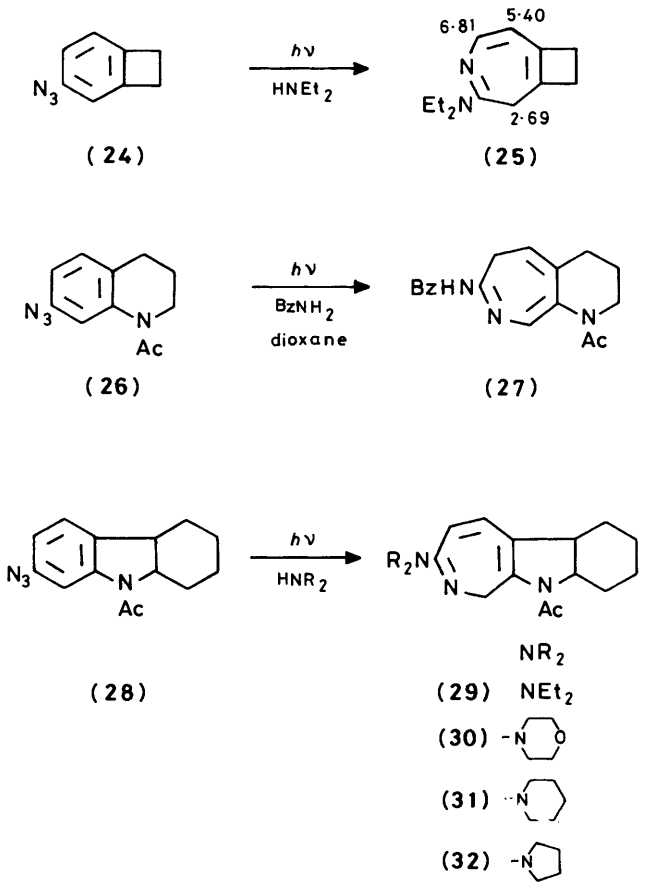


Scheme 5.

containing this mixture resolved an apparent 'doublet' at δ 6.80 into a doublet at δ 6.80 (J 8.0 Hz), coupled to a doublet at δ 5.49 (J 8.0 Hz) [for the major isomer (**22**)], and a singlet at δ 6.85 [for the minor isomer (**23**)].[20] Both the doublet and singlet at δ 6.80 and δ 6.85, respectively, are shifted significantly downfield in the presence of Eu(fod)$_3$ and are, therefore, adjacent to a ring nitrogen atom.

Apart from the results reported already in this paper there are few other literature reports about ring expansions of bicyclic azides (mainly 'β-azides') in which one of the rings is partially saturated. Irradiation of 4-azido-1,2-dihydrobenzocyclobutene (**24**) (Scheme 6) in neat diethylamine gives the cyclobuta[*d*]-azepine (**25**) (55% yield)[20] whilst irradiation of the azidotetrahydroquinoline (**26**) (Scheme 6) in dioxane containing benzylamine gives the pyrido[2,3-*c*]azepine (**27**) (58% yield) whose structure has been confirmed by *X*-ray analysis.[21] Similarly, the partially saturated tricyclic system 9-acetyl-7-azido-1,2,3,4,4a,9a-hexahydrocarbazole (**28**) (Scheme 6) yields the azepino[3,4-*b*]indoles (**29**)—(**32**) (74—76%).[22] Carde and Jones[20] have studied also the behaviour of 4-azidoindan whilst we[22] have previously studied the behaviour of 9-acetyl-5(and 6)-azido-1,2,3,4,4a,9a-hexahydrocarbazole. In compound (**30**) the 7-membered-ring methylene group appears as two doublets at δ 2.45 and 4.62 (J 13 Hz—expected for *gem*-protons) due to the anisotropic effect of the adjacent carbonyl group.[22] For azepines of a similar type, namely (**10**), (**17**), (**18**), (**22**), and (**25**); (**11**) and (**12**); and (**19**), (**20**), and (**23**), the chemical shifts of the 7-membered ring olefinic protons are closely comparable.

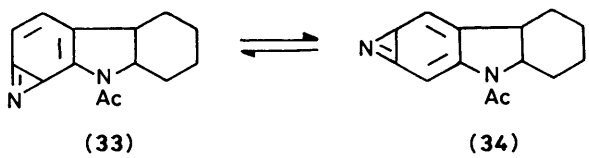
'Bond fixation' appears to be an important factor in controlling the ring expansion of bicyclic azides. Where both rings are aromatic, intermediate azirines such as (**3**) [rather than (**6**), which involves loss of aromaticity in the thiophene ring] are



Scheme 6.

preferred. By contrast, azide (**7**) (Scheme 1) appears to ring-expand *via* an azirine of the opposite type, namely (**8**), arising from the alternative Kekulé structure. There appears also to be a difference between bicyclic systems in which the 'β-isomer' of an azido-substituted benzene ring is annelated to a partially saturated 4- or 5-membered ring and those in which the azido-substituted benzene ring is annelated to a partially saturated 6-membered ring (reminiscent of the 'Mills–Nixon effect'—see below). Thus, from the examples reported so far azides (**7**), (**21**) and (**24**) (all 'β-azides') appear to give azepines of type (**10**), (**22**), and (**25**) as the predominant or sole isolable azepine isomer, whilst azides (**14**) and (**26**) (also 'β-azides') appear to give azepines of type (**19**), (**20**), and (**27**) as the preferred or sole isolable products. The tricyclic system (**28**) appears to prefer to ring-expand *via* intermediate azirine (**33**) rather than the isomeric system (**34**). In all cases equilibria between the two possible azirine systems, *e.g.* (**33**) ⇌ (**34**) or (**8**) ⇌ (**9**), *via* the intermediacy of the precursor nitrene, cannot be ruled out and the products obtained may be those arising from kinetic control of the reactions. These conclusions assume that the azepine products are photochemically stable and the possibility of intermediates of type (**5**) being involved cannot be ruled out.

In 1930, Mills and Nixon[23,24] showed that, by attaching partially saturated C-rings to two *ortho*-valences of a benzene ring, it was possible to demonstrate that the benzene ring could



be made to react as though it had one or other of the two possible Kekulé structures depending on the size of the partially saturated C-ring. According to their proposals small, strained rings annelated to the benzene ring would favour the Kekulé structure resulting in a shared single bond between the two rings whereas larger rings would favour the alternative Kekulé structure. The 'Mills–Nixon effect', which has been the subject of extensive theoretical investigations[25] and which has been extended also to explain the behaviour of benzene rings annelated to partially saturated heterocyclic rings,[26] is now regarded as being too simplistic to explain the behaviour of these different systems. Unequal distributions of electrons ('bond fixation') in the bonds of a benzene ring annelated to a partially saturated carbocyclic or heterocyclic ring, either in the ground state or leading to or going through the transition state,[24] does appear to be dependent on the type of ring annelated and appears to affect the course of the reaction. It is well known that the naphthalene nucleus in its compounds displays bond-fixation properties[27] and benzo[*b*]thiophene compounds are similar in their behaviour.[8,9]

Experimental

I.r. spectra (liquids as films and solids as Nujol mulls between sodium chloride plates) were recorded with a Perkin-Elmer 297 instrument, ^{1}H n.m.r. spectra with either a Perkin-Elmer R32 (90 MHz) or Varian Associates EM360A (60 MHz) instrument ($SiMe_4$ as internal standard in all cases), and mass spectra with a Kratos MS30 instrument. All new compounds gave mass spectra consistent with their proposed structures. Azides were photolysed with a medium-pressure mercury discharge lamp, through a Pyrex filter, emitting light predominantly at 254, 265, 297, 313, and 366 nm.

In all solvent extractions the extracts were combined, dried ($MgSO_4$), and the solvent was distilled on a rotary evaporator. Light petroleum refers to that fraction with b.p. 60—80 °C unless stated otherwise. Chromatography was carried out on alumina (CAMAG 100—250 mesh).

The following compounds were prepared by literature procedures: 2,3-dibromobenzo[*b*]thiophene (84%),[28] m.p. 57—59 °C (from methanol) (lit.,[29] m.p. 57—58 °C), 6-acetyl-2,3-dibromobenzo[*b*]thiophene (33%)[4] [we preferred to steam-distil the nitrobenzene, which left an aqueous suspension of a brown solid. After decantation, the product was extracted with dichloromethane, and trituration of the residue, after removal of the solvent, with light petroleum (b.p. 40—60 °C) gave the product], m.p. 129.5—130 °C [from light petroleum (b.p. 80—100 °C)] (lit., m.p. 131—132 °C[4] and 130—132 °C[29]), 6-acetamido-2,3-dibromobenzo[*b*]thiophene (93%),[29] m.p. 200—202 °C (from ethanol) (lit., 202—204 °C[4] and 200—201 °C[29]), 6-amino-2,3-dibromobenzo[*b*]thiophene hydrochloride (95%)[29] (used without purification), 6-azido-2,3-dibromobenzo[*b*]thiophene (76%),[4] m.p. 119—120 °C (from ethanol) (lit.,[4] 118—119 °C), 2,3-dibromo-6-diethylamino-8*H*-thieno[2,3-*c*]azepine (**11**) (10%)[4] (photolysis time reduced to 7 h in the presence of pyrene), m.p. 110—112 °C (from light petroleum) (lit.,[4] 110—112 °C), benzo[*b*]thiophene 1,1-dioxide (68%), m.p. 139—141 °C (from water) (lit.,[30] 142—143 °C), 6-nitrobenzo[*b*]thiophene 1,1-dioxide (85%), m.p. 186—188 °C (from ethyl acetate) (lit.,[31] 188 °C), and 6-amino-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (75%), m.p. 199—201 °C (from ethanol) (lit.,[7] 203—205 °C).

6-*Amino*-2,3-*dihydrobenzo*[b]*thiophene*.—DIBAL-H (128 ml of a 25% w/w solution in toluene) was added to a stirred suspension of 6-amino-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide (9.15 g, 50.0 mmol) in anhydrous toluene (100 ml) at ambient temperature under nitrogen whereupon the mixture warmed

spontaneously to ~ 50 °C, when it became homogeneous. Then it was stirred at 70 °C for 5 h and a second portion (60 ml) of the DIBAL-H solution was added. The mixture was stirred at this temperature for a further 2 h, then cooled and added slowly to well stirred and cooled (0 °C) 40% aqueous sodium hydroxide (100 ml). Extraction with ether (3 × 150 ml) gave the *title product* (5.47 g, 73%), b.p. (Kugelrohr single-path distillation) 125—130 °C at 0.04—0.1 mmHg; m.p. 69—71 °C; δ($CDCl_3$) 3.20—3.70 (2 H, br s, exchangeable, NH_2), 3.00—3.40 (4 H, m, 2- and 3-H_2), 6.28 (1 H, dd, *J* 2.0 and 9.0 Hz, 5-H), 6.50 (1 H, d, *J* 2.0 Hz, 7-H), and 6.90 (1 H, d, *J* 9.0 Hz, 4-H) (Found: C, 63.3; H, 6.0; N, 9.2. C_8H_9NS requires C, 63.6; H, 6.0; N, 9.3%).

6-*Azido*-2,3-*dihydrobenzo*[b]*thiophene* (**7**).—A solution of sodium nitrite (2.25 g, 32.60 mmol) in water (20 ml) was added dropwise to a stirred solution of 6-amino-2,3-dihydrobenzo[*b*]-thiophene (4.24 g, 28.0 mmol) in a mixture of conc. hydrochloric acid (14 ml) and water (20 ml) at 3—7 °C. The resulting solution was filtered through a Buchner funnel into a Buchner flask, both containing ice, and the filtrate was kept ice-cold during its dropwise addition to a stirred solution of sodium azide (2.12 g, 32.60 mmol) and sodium acetate (11.48 g, 140.0 mmol) in water (80 ml) at ambient temperature. After 15 min the mixture was extracted with ether (3 × 100 ml) to give the *product* (**7**) (4.0 g, 80%) as an oil, b.p. 79—82 °C at 0.02 mmHg (Kugelrohr single-path distillation); $\nu_{max.}$(film) 2 125 cm^{-1} (N_3); δ 3.10—3.40 (4 H, m, 2- and 3-H_2), 6.61 (1 H, dd, *J* 2.0 and 8.0 Hz, 5-H), 6.85 (1 H, d, *J* 2.0 Hz, 7-H), and 7.10 (1 H, d, *J* 8.0 Hz, 4-H) (Found: C, 54.2; H, 4.0; N, 23.7%; M^+, 177. $C_8H_7N_3S$ requires C, 54.3; H, 4.0; N, 23.7%; *M*, 177).

Photolysis of 6-*Azido*-2,3-*dihydrobenzo*[b]*thiophene* (**7**).—A solution of the azide (1.0 g, 5.65 mmol) in a mixture of diethylamine (20 ml) and THF (130 ml) under nitrogen was irradiated for 7 h (azide stretching frequency monitored by i.r.). Distillation of the solvents under reduced pressure gave a dark oil, which was chromatographed on alumina. Light petroleum (b.p. 40—60 °C) (freshly distilled to remove high-boiling components) eluted starting material (0.1 g, 10% recovery) whilst light petroleum (b.p. 40—60 °C)–ether (9:1) eluted 7-*diethylamino*-2,3-*dihydro*-8H-*thieno*[2,3-d]*azepine* (**10**) (0.55 g, 49% based on starting material consumed) as an oil, $\nu_{max.}$ 1 590 cm^{-1} (C=N); δ($CDCl_3$) 1.15 (6 H, t, *J* 7.0 Hz, Me), 2.80—3.10 (4 H, m, 2- and 3-H_2), 3.35 (6 H, m; CH_2Me, q, *J* 7.0 Hz, overlapping with 8-H_2, s), 5.50 (1 H, d, *J* 8.0 Hz, 4-H), and 6.75 (1 H, d, *J* 8.0 Hz, 5-H) (Found: C, 64.9; H, 8.2; N, 12.5%; M^+, 222. $C_{12}H_{18}N_2S$ requires C, 64.9; H, 8.2; N, 12.6%; *M*, 222).

7-*Diethylamino*-8H-*thieno*[2,3-d]*azepine* (**13**).—A solution of bromine in trichloromethane (5% v/v; 5.1 ml, 5.0 mmol) was added dropwise to a stirred solution of 7-diethylamino-2,3-dihydro-8*H*-thieno[2,3-*d*]azepine (**10**) (1.0 g, 4.5 mmol) in a mixture of tetrachloromethane (20 ml) and trichloromethane (5 ml) at ambient temperature. The mixture was stirred for a further 1 h, then added to a stirred excess of aqueous sodium hydrogen carbonate. The organic layer was separated, washed successively with water and brine, and dried ($MgSO_4$). Distillation of the solvents under reduced pressure gave a residue, which was chromatographed on alumina. Light petroleum (b.p. 40—60 °C) (freshly distilled)–ether (9:1) eluted the thienoazepine (**13**) (0.3 g, 30%). After two recrystallisations from light petroleum (b.p. 40—60 °C) the *title product* (0.07 g, 7%) had m.p. 56.5—57.5 °C; δ($CDCl_3$) 1.18 (6 H, t, *J* 7.0 Hz, Me), 3.37 (2 H, s, 8-H_2), 3.43 (4 H, q, *J* 7.0 Hz, CH_2Me), 6.22 (1 H, d, *J* 8.0 Hz, 4-H), 6.94 (1 H, d, *J* 5.0 Hz, 3-H), 7.05 (1 H, d, *J* 8.0 Hz, 5-H), and 7.09 (1 H, d, *J* 5.0 Hz, 2-H) (Found: C, 65.45; H, 7.35; N, 12.75. $C_{12}H_{16}N_2S$ requires C, 65.5; H, 7.3; N, 12.7%).

6-*Diethylamino*-8H-*thieno*[2,3-c]*azepine* (**12**).—1.69M Butyllithium in hexane (1.89 ml, 3.2 mmol) was added dropwise to a stirred solution of 2,3-dibromo-6-diethylamino-8*H*-thieno-[2,3-*c*]azepine (**11**) (0.55 g, 1.45 mmol) in anhydrous ether (25 ml) at −75 °C under nitrogen. The mixture was stirred for a further 45 min at this temperature, then allowed to warm to −65 °C at which temperature it was stirred for 15 min. Water (2 ml) was added and, after 15 min, the mixture was warmed up to ambient temperature. The ethereal layer was washed with water (3 × 10 ml), dried ($MgSO_4$), and distilled under reduced pressure to give a residue, which was chromatographed on alumina. Ether–light petroleum (b.p. 40—60 °C) (1:9) eluted starting material (0.18 g, 32% recovery) whilst ether eluted the *title product* (**12**) (0.08 g, 37% based on starting material consumed) as a pale yellow oil, $\nu_{max.}$(film) 1 590 cm^{-1} (C=N); δ($CDCl_3$) 1.10 (6 H, t, *J* 7.0 Hz, Me), 3.27 (4 H, q, *J* 7.0 Hz, CH_2Me), 4.25 (2 H, s, 8-H_2), 6.56 (1 H, d, *J* 12.0 Hz, 4-H), 7.03 (2 H, dd, *J* 6.0 Hz, 2- and 3-H), and 7.14 (1 H, d, *J* 12.0 Hz, 5-H) (Found: C, 65.35; H, 7.2; H, 12.9. $C_{12}H_{16}N_2S$ requires C, 65.5; H, 7.3; N, 12.7%).

6-*Acetyl*-1,2,3,4-*tetrahydronaphthalene*.—Freshly distilled 1,2,3,4-tetrahydronaphthalene (41.0 g, 43 ml, 0.31 mol) was added dropwise to a stirred, chilled (0 °C) mixture of aluminium chloride (45.0 g, 0.33 mol) and nitrobenzene (100 ml); acetyl chloride (27.6 g, 25 ml, 0.35 mol) was then added. The cooling bath was removed and the mixture was allowed to warm to ambient temperature during 2 h. Then it was added slowly to vigorously stirred dil. hydrochloric acid [conc. hydrochloric acid (100 ml), water (50 ml), and crushed ice (50 ml)] and the nitrobenzene was steam-distilled off. Extraction of the residue with dichloromethane gave 6-acetyl-1,2,3,4-tetrahydronaphthalene (53 g, 98%), b.p. 100—120 °C at 1 mmHg (lit.,[17] 161 °C at 16 mmHg); $\nu_{max.}$ 1 680 cm^{-1} (CO); δ($CDCl_3$) 1.64—1.96 (4 H, m, 2-and 3-H_2), 2.50 (3 H, s, Me), 2.60—2.95 (4 H, m, 1- and 4-H_2), 7.10 (1 H, d, *J* 8.0 Hz, 8-H), and 7.65 (2 H, m, 5- and 7-H), which was used without further purification.

6-*Acetamido*-1,2,3,4-*tetrahydronaphthalene*.—Conc. sulphuric acid (25 ml) was added dropwise from a Pasteur pipette to a stirred solution of 6-acetyl-1,2,3,4-tetrahydronaphthalene (8.14 g, 46.7 mmol) and sodium azide (12.16 g, 187.0 mmol) in glacial acetic acid (250 ml) initially at 65 °C (during the addition the temperature increased to *ca.* 105 °C) (**CAUTION**: hydrazoic acid is generated!); the resulting mixture was cooled and poured into water (250 ml). Long needles of the title product (2.76 g, 31%) separated out from the mixture overnight and were filtered off, m.p. 104—105 °C (lit.,[18] 107 °C); $\nu_{max.}$ 3 270 (NH) and 1 655 cm^{-1} (CO); δ($CDCl_3$) 1.66—2.00 (4 H, m, 2- and 3-H_2), 2.16 (3 H, s, Me), 2.60—2.90 (4 H, m, 1- and 4-H_2), 7.00 (1 H, d, *J* 8.0 Hz, 8-H), 7.23 (1 H, d, *J* 8.0 Hz, 7-H), 7.30 (1 H, s, 5-H), and 8.00 (1 H, br s, exchangeable, NH). A further quantity (4.34 g) of less pure material was obtained by extraction with ether (total yield 7.1 g, 80%).

6-*Amino*-1,2,3,4-*tetrahydronaphthalene*.—A mixture of 6-acetamido-1,2,3,4-tetrahydronaphthalene (7.10 g, 37.5 mmol), methanol (50 ml), and potassium hydroxide (20 g, 35.7 mmol) was heated under reflux for 24 h, then cooled, and poured into water (800 ml). Extraction with ether gave the title product as an oil (4.5 g, 81.5%), b.p. 190—195 °C at 25 mmHg (lit.,[18] 147—148 °C at 13 mmHg).

6-*Azido*-1,2,3,4-*tetrahydronaphthalene* (**14**) (80%) was prepared in a manner similar to that described before for the synthesis of 6-azido-2,3-dihydrobenzo[*b*]thiophene. It had b.p. 90—95 °C at 0.3 mmHg (Kugelrohr single-path distillation); $\nu_{max.}$ 2 125 cm^{-1} (N_3); δ($CDCl_3$) 1.60—1.90 (4 H, m, 2- and 3-H_2), 2.50—2.90 (4 H, m, 1- and 4-H_2), 6.55—6.80 (2 H, m, 5- and

7-H), and 6.95 (1 H, d, *J* 9.0 Hz, 8-H) (Found: C, 69.4; H, 6.3; N, 24.4. $C_{10}H_{11}N_3$ requires C, 69.4; H, 6.4; N, 24.3%).

Photolysis of 6-*Azido*-1,2,3,4-*tetrahydronaphthalene* (**14**).—(a) *In diethylamine–THF.* A solution of the azide (1.0 g, 5.8 mmol) and diethylamine (15 ml) in THF (135 ml) was irradiated at ambient temperature for 7 h. Removal of the solvent and the excess of diethylamine and two distillations (Kugelrohr single-path distillation) of the residue gave a mobile oil (0.6 g, 48%), b.p. 160—170 °C at 1.2 mmHg, which was shown by ^{1}H n.m.r. spectroscopic analysis to be a mixture of the following azepines in a 5:1 ratio: 3-*diethylamino*-6,7,8,9-*tetrahydro*-4H-2-*benzazepine* (**19**) (major isomer); δ($CDCl_3$) 1.16 (6 H, t, *J* 7.0 Hz, Me), 1.50—1.85 (4 H, m, 7- and 8-H_2), 2.10—2.80 (6 H, m, 4-, 6-, and 9-H_2), 3.33 (4 H, q, *J* 7.0 Hz, CH_2Me), 4.86 (1 H, t, *J* 8.0 Hz, 5-H), and 6.83 (1 H, s, 1-H); and 2-*diethylamino*-6,7,8,9-*tetrahydro*-1H-3-*benzazepine* (**17**) (minor isomer); δ($CDCl_3$) 1.16 (6 H, t, *J* 7.0 Hz, Me), 1.50—1.85 (4 H, m, 7- and 8-H_2), 2.10—2.80 (6 H, m, 1-, 6-, and 9-H_2), 3.31 (4 H, q, *J* 7.0 Hz, CH_2Me), 5.6 (1 H, d, *J* 9.0 Hz, 5-H), and 6.87 (1 H, d, *J* 9.0 Hz, 4-H).

(b) *In morpholine–THF.* A solution of the azide (**14**) (1.0 g, 5.8 mmol) and morpholine (15 ml) in THF (135 ml) was irradiated for 7 h. Removal of the solvent and the excess of morpholine (by high-vacuum distillation) left a residue, which was dissolved in methanol (15 ml). Acetic anhyhdride (5.41 g, 5 ml, 53.0 mmol) was added to this chilled (0 °C) solution followed, after 30 min, by water (150 ml). The aqueous layer was extracted with ethyl acetate (3 × 50 ml), treated with sodium hydrogen carbonate to adjust the pH to 8—9, and re-extracted with dichloromethane; the latter extract gave a residue, which was distilled (Kugelrohr single-path distillation) twice to give a mixture (0.53 g, 39.5%) (Found: C, 71.8; H, 8.6; N, 11.7. $C_{14}H_{20}N_2O$ requires C, 72.5; H, 8.7; N, 12.1%), b.p. 165—170 °C at 0.8 mmHg, of two azepines in the ratio 85:15:3-*morpholino*-6,7,8,9-*tetrahydro*-4H-2-*benzazepine* (20) (major isomer); δ($CDCl_3$) 1.50—1.80 (4 H, m, 7- and 8-H_2), 2.10—2.80 (6 H, m, 4-, 6-, and 9-H_2), 3.37 (4 H, t, *J* 7.0 Hz, 2 × CH_2), 3.65 (4 H, t, *J* 7.0 Hz, 2 × CH_2), 4.86 (1 H, t, *J* 8.0 Hz, 5-H), and 6.83 (1 H, s, 1-H); and 2-*morpholino*-6,7,8,9-*tetrahydro*-1H-3-*benzazepine* (**18**); δ($CDCl_3$) 1.50—1.80 (4 H, 7- and 8-H_2), 2.10—2.80 (6 H, m, 1-, 6-, and 9-H_2), 3.37 (4 H, t, *J* 7.0 Hz, 2 × CH_2), 3.65 (4 H, t, *J* 7.0 Hz, 2 × CH_2), 5.63 (1 H, d, *J* 9.0 Hz, 5-H), and 6.88 (1 H, d, *J* 9.0 Hz, 4-H).

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