Journal of Organometallic Chemistry 695 (2010) 2673–2678

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Formation of a new ring system: Tetrazolo[5,1-*f*][1,2]azaborinin

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ARTICLE INFO

Article history:
Received 26 March 2010
Received in revised form
11 August 2010
Accepted 13 August 2010
Available online 1 October 2010

Keywords:
Phenothiazine
Cyclization
Azaborinin
Solid-state NMR
Single crystal
X-ray

ABSTRACT

Phenothiazinyldienes obtained from tetrazolopyridinium salts and phenothiazine derivatives were subjected to reduction by borane–dimethyl sulfide in THF. Structure elucidation of the products revealed that one of the olefinic bond underwent reduction and, furthermore, borane addition at the double bond took place to yield derivatives of tetrazolo[5,1-*f*][1,2]azaborinin as a new fused ring system involving a bridge-head nitrogen atom. The new products have been synthesized and characterized by X-ray analysis, solution and solid-state NMR.

1. Introduction

Earlier we have reported that reaction of the easily accessible tetrazolo[1,5-*a*]pyridinium salts [1] (**1**) with phenothiazine (**2**) affords *N*-dienylphenothiazines bearing substituted tetrazole moiety at the end of the diene chain (**3**, Scheme 1) [2]. Because of valuable biological properties of some related phenothiazines substituted by saturated carbon chains on the thiazine-nitrogen atom [3], we have now decided to reduce the dienyl moieties of these derivatives in order to seek for novel biologically active compounds. Because of the presence of the sulfur atom, catalytic hydrogenation had to be ruled out and, thus, the transformation was tried by the use of borane–dimethyl sulfide complex as the reducing agent [4]. This reagent has recently been applied successfully for hydrogenation of enamines [5].

2. Results and discussion

When dienylphenothiazines (**3a**–**d**) were treated with the borane reagent under mild conditions (0 °C) in tetrahydrofurane, total disappearance of the starting compound was monitored by tlc after 3 h. Formation of one main product was experienced which was isolated by chromatography and was obtained in moderate (22–33%) yield. Mass spectroscopy and elemental analysis revealed, interestingly, that the product molecules contain a boron atom. The stability of these crystalline products suggested that the boron content was incorporated highly probably by covalent bonds.

In the possession of appropriate single crystals of the reduction product obtained from **3b**, X-ray diffraction analysis was carried out in order to elucidate the structure: it has shown that in the course of this transformation a BH_2 group was attached to C2 of the carbon chain followed by formation of a B–N σ-bond with participation of the adjacent ring-nitrogen atom of the tetrazole ring. Thus, a zwitterionic derivative of a bridge-head nitrogen containing new heterocyclic ring system: tetrazolo[5,1-*f*][1,2]azaborinin (**4b**) was formed (Scheme 2).

The reaction obviously proceeds *via* formation of a boron-containing intermediate (**A**) which is formed by borane addition to the double bond C1–C2. The easy formation of **4** is due to the proximity of the BH_2 group and the N atom of the tetrazole ring. In the course of this reaction the olefinic C3–C4 bond was also reduced.

The single crystal X-ray diffraction analysis proved that there is one molecule in the asymmetric unit of **4b** (Fig. 1.). It crystallises in the monoclinic crystal system, space group $P2_1/n$. Although the lattice parameters feature higher symmetry as β angle is close to 90° indicating the possibility of orthorhombic crystal system, it is not supported by the content of the unit cell. There is one chiral atom in the molecule, it is the carbon bonded toward the

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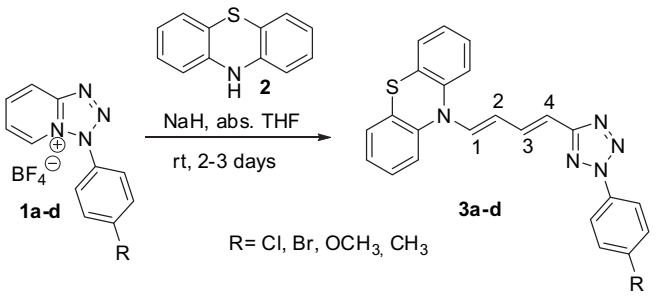
doi:10.1016/j.jorganchem.2010.08.049



Scheme 1.

phenothiazine in the ring containing the B. Both enantiomers can be found in the centrosymmetric cell.

The diffraction measurement was performed at low temperature, −180 °C. The structure was ordered. All hydrogen atoms were found on difference Fourier maps. It was possible to refine the structure to $R = 2.87\%$. Packing diagrams with the view from the *a*, *b* and *c* crystallographic axis are shown in ESI Fig. S1.

There are no classic hydrogen bonds in the crystal structure. There is one shorter centroid–centroid distance only: between C2–C3–C4–C5–C6–C7 rings with the intermolecular [1 − *X*,1 − *Y*,1 − *Z*] distance of 3.7716(11) Å. All other ring distances are over 4 Å. Furthermore, two C–H…π interactions can be found in the crystal structure: C4–H4…C8–C9–C10–C11–C12–C13 ring [1 − *X*,1 − *Y*,1 − *Z*] 2.95 Å 134° and C32–H32…C2–C3–C4––C6–C5C7 [−*X*,−*Y*,1 − *Z*].

Our literature survey revealed that very few azaborinins related to **4** have been described in the literature [7,8] and, furthermore, no fused azaborinin with bridge-head nitrogen atom has been reported. Thus, these zwitterionic tetrazolo[5,1-*f*][1,2]azaborinin derivatives (**4**) represent a new unprecedented ring system.

The comparison of solution and solid-state NMR data was useful to confirm the formation of the new heterocyclic ring system **4a**–**d**. Chloroform solution of **4b** was investigated to determine the boron-containing six-membered ring in solution. The *J*-coupling patterns of the diastereotopic methylene protons attached to C7 and C8 carbons suggested the intramolecular ring formation (Fig. 2). The homonuclear couplings of the boron-attached protons ($^3J_{\underline{B}Hax\text{-}H6} = 6.0$ Hz and $^3J_{\underline{B}Heq\text{-}H6} = 4.0$ Hz) are also characteristic of the six-membered ring system (ESI Fig. S3). In addition, solid-state NMR spectroscopy was applied to provide a link between the structure of **4b** determined by single crystal X-ray diffraction and the solution NMR data. The isotropic chemical shifts (δ_{iso}) obtained from ^{11}B-MAS (Fig. 3.) and ^{13}C-CP/MAS (ESI Fig. S4) are in good agreement with the δ_{10B} and δ_{13C} chemical shifts measured in $CDCl_3$. Therefore, we conclude that the solution structure of **4b** is identical to that determined by single crystal X-ray diffraction. The close similarity of the proton (ESI Figs. S2 and S3), carbon (ESI Figs. S4–S7) and boron NMR spectra (ESI Figs. S8 and S9) of **4a**,**c**,**d** to those of the fully characterized **4b** clearly shows that all these derivatives have related structures both in solution and in solid state.

An interesting feature of the solid-state ^{13}C-CP/MAS spectra of the new products (**4a**–**d**) is that certain resonances are doubled in the aromatic region as compared to the solution spectra (ESI Figs. S4–S7).

In the case of **4b** the single resonance at 146.2 ppm represents both nitrogen attached quaternary carbons of the phenothiazine ring (C-9a″/C-10a″) in $CDCl_3$. This, however, splits into two clearly non-equivalent carbon sites ($\delta_{iso} = 149.0$ and 144.0 ppm) in the solid-state ^{13}C-CP/MAS spectrum. As a consequence of the asymmetric structure, the two sets of aromatic carbons in the phenothiazine moiety experience different magnetic shielding. This, in turn, remains hidden behind rapid chemical exchange processes in solution due to the conformational flexibility of the phenothiazine moiety.

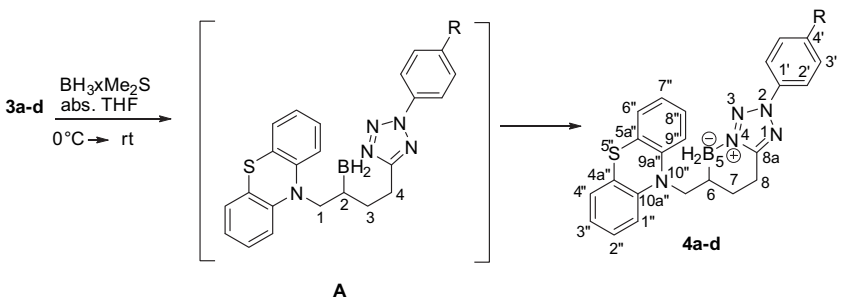
Exploration of reactivity of the new zwitterionic azaborinin derivative as well as extension of reductive transformations of phenothiazinyldienes is in progress.

3. Experimental

3.1. General

Melting Points were determined on a Büchi apparatus and are uncorrected. The IR spectra were recorded on a Thermo Nicolet Avatar 320 FT-IR spectrometer. The elemental analysis has been carried out with an Elementar Vario EL III apparatus (at the Analytical Laboratory for Organic Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri út 59–67). All the chemicals and solvents were used as supplied.

NMR experiments were carried out on 400 MHz (for ^{1}H) and 600 MHz (for ^{1}H) Varian NMR SYSTEM spectrometers by using 5 mm direct detection ^{15}N–^{31}P/{^{1}H–^{19}F} probes equipped with Z pulse field gradient. The assignments of the resonances of **4a**–**d** followed the regular procedure: collection and analysis of selective 1D TOCSY, selective 1D NOESY and heteronuclear through-bond correlations (^{1}H–^{13}C–gHSQC and ^{1}H–^{13}C–gHMBC). Measurements were performed at +25 °C in $CDCl_3$. ^{1}H and ^{13}C NMR spectra are referenced to residual solvent signal ($\delta_H = 7.24$ ppm; $\delta_C = 77.0$ ppm). Et_2OxBF_3 in $CDCl_3$ was used as external reference for ^{10}B{^{1}H} NMR spectra. The direct detection of ^{10}B instead of the commonly used ^{11}B was chosen to avoid the strong background of the latter. The rapid relaxation of the boron nuclei in the asymmetric environment (**4a**–**d**) leads to extremely broad resonances (see ESI Fig. S8), which are difficult to detect. ^{1}H{^{11}B} NMR spectra were recorded by using broadband



Scheme 2.

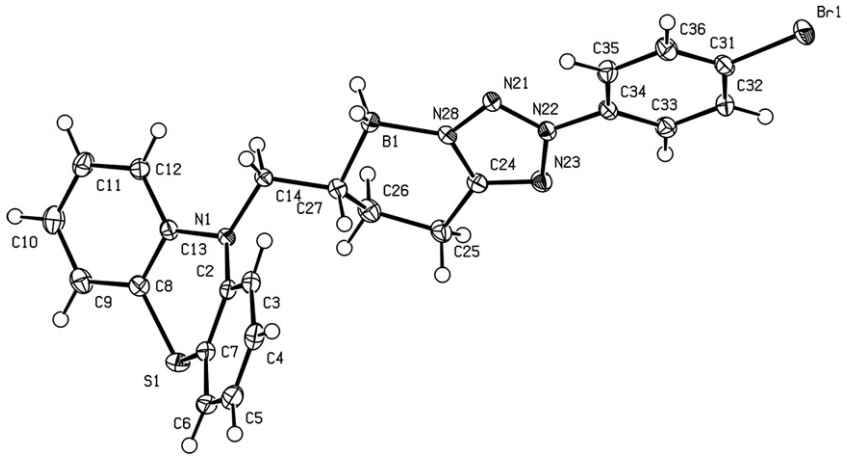


Fig. 1. Molecular structure ORTEP [6] representation of **4b**. The displacement ellipsoids are drawn at 50% probability level, hetero atoms are shaded.

decoupling [11]. Solid-state ^{11}B-MAS and ^{13}C-CP/MAS spectra were recorded on 400 MHz (for ^{1}H) Varian NMR SYSTEM spectrometer by using a 4.0 mm HX Varian Chemagnetics MAS probe and on 600 MHz (for ^{1}H) Varian NMR SYSTEM spectrometer by using a 3.2 mm HXY Varian Chemagnetics MAS probe. Chemical shifts in the solid state were referenced to Et_2OxBF_3 in $CDCl_3$ ($\delta_{11B} = 0$ ppm) for boron and to adamantane ($\delta_{13C} = 38.55$, 29.50 ppm) for carbon. Recycle delays 600 s for **4a**–**b** and 10 s for **4c**–**d** were used in the ^{13}C-CP/MAS experiments (1–2 ms contact time, 92 kHz TPPM proton decoupling). ^{11}B-MAS experiments (92 kHz TPPM proton decoupling) were recorded with 10–60 s recycle delays.

3.2. Experimental procedures and spectroscopic data

3.2.1. General procedure for preparation of tetrazolyldienylphenothiazines (*3a*–*d*)

To a mixture of sodium hydride (60%, 0.26 g, 6.67 mmol) and phenothiazine **2** (1.21 g, 6.06 mmol) in abs. THF (50 cm^3) was added dropwise the appropriate 3*H*-tetrazolo[1,5-*a*]pyridin-4-ium **1a**–**d** (5.51 mmol) over 20 min, and the mixture was stirred at room temperature for 2 days. After evaporation of reaction mixture the residue was dissolved with EtOAc:water = 1:1 eluent (50 cm^3) and the solid product was filtered off. The aqueous mother liquor was extracted with EtOAc (thrice) and the organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated. The combined organic solvent was evaporated, the residue was washed with diethyl ether then it was recrystallised from ethyl acetate to give **3a**–**d**.

*3.2.1.1. 10-((1E,3E)-4-(2-(4-Chlorophenyl)-2H-tetrazol-5-yl)buta-1,3-dien-1-yl)-10H-phenothiazine (**3a**).* Starting from 3-(4-chlorophenyl)-3*H*-tetrazolo[1,5-*a*]pyridin-4-ium **1a** (1.75 g, 5.51 mmol) to give **3a** (1.91 g, 81%) was filtered off as yellow crystals (mp 198–202 °C); (Found: N, 16.29; C, 64.32; H, 3.40; $C_{23}H_{16}ClN_5S$ requires N, 16.29; C, 64.25; H, 3.75%); ν_{max}(KBr)/cm^{-1} 1622, 1500, 1257, 994 and 766; δ_H (300 MHz, $CDCl_3$; Me_4Si) 6.19 (1H, d, $J = 11.4$ Hz), 6.65 (1H, t, $J = 11.4$ Hz), 7.18–7.24 (3H, m), 7.31–7.37 (4H, m), 7.48–7.57 (4H, m), 7.66 (1H, dd, $J = 13.8$, 11.4 Hz), 7.989 (2H, m); δ_C (75 MHz, $CDCl_3$; Me_4Si) 103.5, 105.7, 120.7 (2C), 122.4 (2C), 125.6 (2C), 127.4 (2C), 128.1 (2C), 129.6 (2C), 130.6, 135.0, 136.7, 139.8, 141.2, 141.5, 164.8; *m*/*z* (EI) 429.0824 ($C_{23}H_{16}ClN_5S$ requires 429.0815), 401 (25%), 276 (52), 262 (68), 199 (86), 198 (100), 167 (30), 154 (10), 140 (8), 127 (16), 90 (8), 77 (5) and 63 (10).

*3.2.1.2. 10-((1E,3E)-4-(2-(4-Bromophenyl)-2H-tetrazol-5-yl)buta-1,3-dien-1-yl)-10H-phenothiazine (**3b**).* Starting from 3-(4-bromophenyl)-3*H*-tetrazolo[1,5-*a*]pyridin-4-ium **1a** (2.00 g, 5.51 mmol) to give **3b** (1.98 g, 76%) as yellow crystals (mp 200–204 °C); (Found: N, 14.55; C, 57.91; H, 3.11; $C_{23}H_{16}BrN_5S$ requires N, 14.76; C, 58.23; H, 3.40%); ν_{max}(KBr)/cm^{-1} 1621, 1499, 1257, 994 and 765; δ_H (300 MHz, $CDCl_3$; Me_4Si) 6.19 (1H, d, $J = 11.1$ Hz), 6.65 (1H, t,

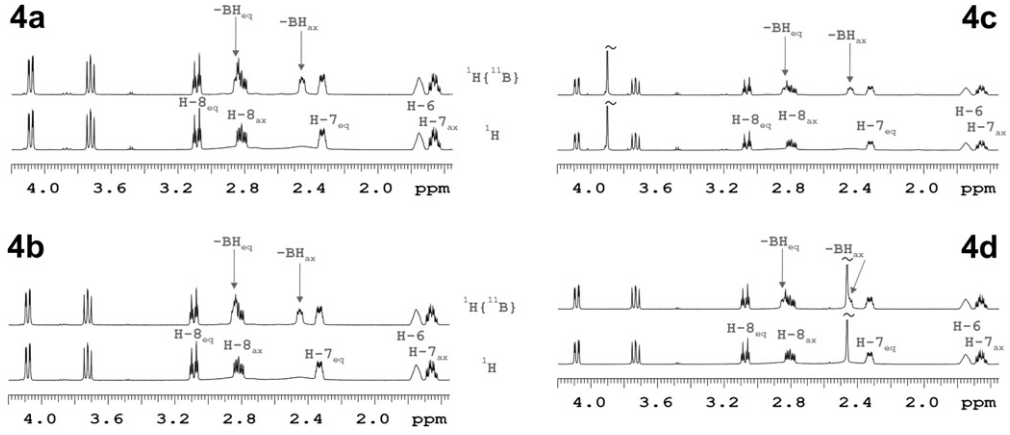


Fig. 2. Aliphatic region of the ^{1}H and ^{1}H{^{11}B} NMR spectra of **4a**–**d** in $CDCl_3$. The resonances of the boron-attached protons are indicated by arrows.

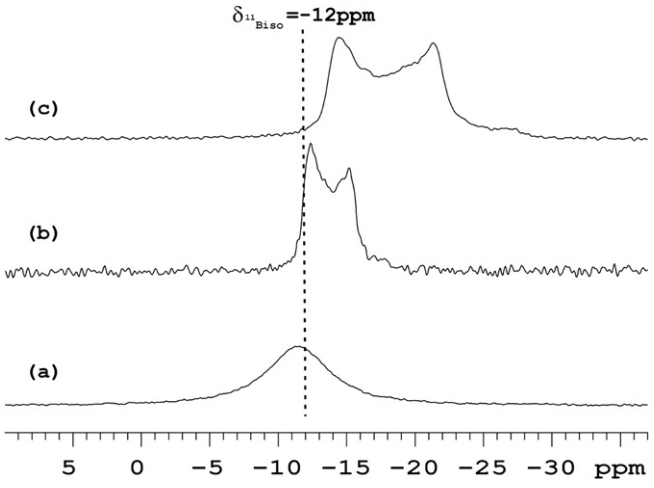


Fig. 3. Solution and solid-state boron NMR spectra of **4b**. (a) $^{10}B\{^1H\}$ in $CDCl_3$ (b) $^{11}B\{^1H\}$-MAS [9] at 192.4 MHz, 7 kHz (c) $^{11}B\{^1H\}$-MAS at 128.3 MHz, 7 kHz. The isotropic chemical shift was determined by using the SIMPSON package [10].

$J = 11.1$ Hz), 7.17–7.23 (3H, m), 7.30–7.37 (4H, m), 7.55 (2H, d, $J = 7.2$ Hz), 7.61–7.66 (3H, m), 7.92 (2H, m); δ_C (75 MHz, $CDCl_3$; Me_4Si) 103.5, 105.6, 120.9 (2C), 122.4 (2C), 125.6 (2C), 127.4 (2C), 128.1 (2C), 130.6, 132.6 (2C), 136.8, 137.7, 139.8, 141.2, 141.5, 164.8; *m/z* (EI) 473.0314 ($C_{23}H_{16}BrN_5S$ requires 473.0310), 447 (8%), 276 (16), 262 (23), 248 (15), 199 (100), 167 (40), 154 (9), 99 (5), 77 (6) and 63 (9).

*3.2.1.3. 10-((1E,3E)-4-(2-(4-Methoxyphenyl)-2H-tetrazol-5-yl)buta-1,3-dien-1-yl)-10H-phenothiazine (**3c**).* Starting from 3-(4-methoxyphenyl)-3*H*-tetrazolo[1,5-*a*]pyridin-4-ium **1c** (1.73 g, 5.51 mmol) to give **3c** (1.73 g, 74%) as yellow-brown crystals (mp 194–199 °C); (Found: N, 16.30; C, 67.60; H, 4.32; $C_{24}H_{19}N_5OS$ requires N, 16.46; C, 67.74; H, 4.50%); ν_{max}(KBr)/cm^{-1} 2360, 1620, 1514, 1257 and 762; δ_H (300 MHz, $CDCl_3$; Me_4Si) 3.90 (3H, s), 6.19 (1H, d, $J = 11.1$ Hz), 6.61 (1H, t, $J = 11.4$ Hz), 7.02 (2H, m), 7.15–7.21 (3H, m), 7.31–7.36 (4H, m), 7.54 (2H, m), 7.69 (1H, dd, $J = 13.8, 11.1$ Hz), 7.96 (2H, m); δ_C (75 MHz, $CDCl_3$; Me_4Si) 55.7, 103.7, 106.2, 114.5 (2C), 121.1 (2C), 122.1, 122.4 (2C), 125.5 (2C), 127.5 (2C), 128.1 (2C), 130.5, 136.1, 140.7, 141.6, 160.2, 164.5; *m/z* (EI) 425.1320 ($C_{24}H_{19}N_5OS$ requires 425.1310) 397 (30%), 276 (78), 262 (51), 227 (70), 198 (100), 167 (16), 121 (51), 106 (17), 91 (8), 78 (13) and 55 (11).

*3.2.1.4. 10-((1E,3E)-4-(2-(p-Tolyl)-2H-tetrazol-5-yl)buta-1,3-dien-1-yl)-10H-phenothiazine (**3d**).* Starting from 3-(*p*-tolyl)-3*H*-tetrazolo [1,5-*a*]pyridin-4-ium **1d** (1.64 g, 5.51 mmol) to give **3d** (1.83 g, 81%) as yellow crystals (mp 203–209 °C); (Found: N, 16.90; C, 70.16; H, 4.55; $C_{24}H_{19}N_5S$ requires N, 17.10; C, 70.39; H, 4.68%); ν_{max}(KBr)/cm^{-1} 1622, 1584, 1463, 1258 and 763; δ_H (300 MHz, $CDCl_3$; Me_4Si) 2.45 (3H, s), 6.20 (1H, d, $J = 11.1$ Hz), 6.62 (1H, t, $J = 11.1$ Hz), 7.16–7.22 (4H, m), 7.29–7.36 (5H, m), 7.53–7.57 (2H, m), 7.69 (1H, dd, $J = 13.8, 11.1$ Hz), 7.92 (2H, m); δ_C (75 MHz, $CDCl_3$; Me_4Si) 21.2, 103.6, 106.1, 119.4 (2C), 122.4 (2C), 125.5 (2C), 127.4 (2C), 128.0 (2C), 129.9 (2C), 130.5, 134.7, 136.2, 139.4, 140.8, 141.5, 164.5; *m/z* (EI) 409.1352 ($C_{24}H_{19}N_5S$ requires 409.1361) 381 (22%), 276 (56), 275 (13), 262 (56), 211 (60), 198 (100), 182 (15), 167 (21), 154 (8), 105 (9), 77 (9) and 69 (10).

*3.2.2. General procedure for preparation of 5,6,7,8-tetrahydro-2H-tetrazolo[5,1-f][1,2]azaborinin-4-ium-5-uides (**4a**–**d**)*

In an inert atmosphere at 0 °C, BH_3xMe_2S (0.4 cm^3, 4 mmol) was added to the suspension of the appropriate tetrazolyldienylphenothiazines (**3a**–**d**, 1 mmol) and abs. THF (10 cm^3). After injection of BH_3xMe_2S, the mixture was stirred from 0 °C to room temperature for 3 h. During this time, the starting suspension turned to be a clear solution. This mixture was cooled to 0 °C and the excess of BH_3xMe_2S was quenched with cold water (10 cm^3). Then the reaction mixture was made alkaline with sodium carbonate solution (10%) and extracted with DCM (15 cm^3, thrice). The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure at room temperature. The residue was purified with flash chromatography on silica gel (gradient from hexane:DCM = 2:1). The solid product was recrystallised from hexane and diethyl ether to give **4a**–**d** as yellow or yellow-white crystals.

*3.2.2.1. 6-((10H-Phenothiazin-10-yl)methyl)-2-(4-chlorophenyl)-5,6,7,8-tetrahydro-2H-tetrazolo[5,1-f][1,2]azaborinin-4-ium-5-uide (**4a**).* Starting from 10-((1*E*,3*E*)-4-(2-(4-chlorophenyl)-2*H*-tetrazol-5-yl)buta-1,3-dien-1-yl)-10*H*-phenothiazine (**3a**, 0.43 g, 1 mmol) to give **4a** (0.11 g, 25%) as yellow crystals (mp 166–168 °C); (Found: N, 15.47; C, 61.86; H, 4.64; $C_{23}H_{21}BClN_5S$ requires N, 15.71; C, 61.97; H, 4.75%); ν_{max}(KBr)/cm^{-1} 3440, 2352, 1452, 1109 and 755; NMR data (+25 °C, $CDCl_3$, 30 mM): $\delta_{1H\text{-}\{11B\}}$ (599.7 MHz) 1.65 (1H, dddd, $J = 12.7, 10.5, 10.3, 4.8, 7_{ax}$-H), 1.74 (1H, br m, 6-H), 2.32 (1H, dddd, $J = 12.7, 5.6, 4.9, 3.1, 7_e$-H), 2.44 (1H, dd, $J = 10.7, 5.7, BH_{ax}$), 2.81 (1H, ddd, $J = 17.6, 10.3, 5.6, 8_{ax}$-H), 2.83 (1H, dd, $J = 10.7, 4.2, BH_{eq}$), 3.07 (1H, ddd, $J = 17.6, 4.9, 4.8, 8_e$-H), 3.71 (1H, dd, $J = 14.0, 11.9, \alpha_1$-H), 4.07 (1H, dd, $J = 14.0, 3.0, \alpha_2$-H), 6.88 (2H, td, $J = 7.7, 1.1, 3''$-H + $7''$-H), 6.98 (2H, dd, $J = 8.1, 1.1, 1''$-H + $9''$-H), 7.12 (2H, ddd, $J = 8.1, 7.7, 1.4, 2''$-H + $8''$-H), 7.14 (2H, dd, $J = 7.7, 1.4, 4''$-H + $6''$-H), 7.57 (2H, m, $3'$-H + $5'$-H), 8.06 (2H, m, $2'$-H + $6'$-H); δ_C (150.8 MHz) 21.8 (6-C), 22.2 (8-C), 25.1 (7-C), 51.6 (α-C), 116.3 ($1''$-C + $9''$-C), 121.4 ($2'$-C + $6'$-C), 122.0 ($3''$-C + $7''$-C), 125.3 ($4a''$-C + $5a''$-C), 127.1 ($2''$-C + $8''$-C), 127.3 ($4''$-C + $6''$-C), 130.3 ($3'$-C + $5'$-C), 134.1 ($1'$-C), 137.7 ($4'$-C), 146.2 ($9a''$-C + $10a''$-C), 162.4 (8a-C); δ_{10B} (64.4 MHz) −11.6 (br s, BH_2); $\delta_{C,iso}$ ($^{13}C\{^1H\}$-CP/MAS; 100.6 MHz; 7 kHz) 22.5, 26.1, 51.5, 117.9, 120.7, 122.5, 123.8, 126.9, 128.4, 133.5, 143.4, 148.9, 162.9; *m/z* (ESI+) $[M + Na]^+$: 468.2, $[M + H]^+$: 446.2 ($C_{23}H_{21}BClN_5S$ requires 445.78).

*3.2.2.2. 6-((10H-Phenothiazin-10-yl)methyl)-2-(4-bromophenyl)-5,6,7,8-tetrahydro-2H-tetrazolo[5,1-f][1,2]azaborinin-4-ium-5-uide (**4b**).* Starting from 10-((1*E*,3*E*)-4-(2-(4-bromophenyl)-2*H*-tetrazol-5-yl)buta-1,3-dien-1-yl)-10*H*-phenothiazine (**3b**) (0.474 g, 1 mmol) to give **4b** (0.160 g, 33%) as yellow crystals (mp 155–157 °C); (Found: N, 14.03; C, 56.30; H, 4.18; $C_{23}H_{21}BBrN_5S$ requires N, 14.29; C, 56.35; H, 4.33%); ν_{max}(KBr)/cm^{-1} 3446, 2354, 1451, 1109 and 755; NMR data (+25 °C, $CDCl_3$, 30 mM): $\delta_{1H\text{-}\{11B\}}$ (599.7 MHz; +25 °C; $CDCl_3$; 20 mM) 1.64 (1H, dddd, $J = 13.0, 10.5, 10.3, 4.9, 7_{ax}$-H), 1.74 (1H, br m, 6-H), 2.33 (1H, dddd, $J = 13.0, 5.7, 4.9, 3.7, 7_e$-H), 2.44 (1H, dd, $J = 10.7, 6.0, BH_{ax}$), 2.81 (1H, ddd, $J = 17.6, 10.3, 5.7, 8_{ax}$-H), 2.83 (1H, dd, $J = 10.7, 4.0, BH_{eq}$), 3.08 (1H, dt, $J = 17.6, 4.9, 8_e$-H), 3.71 (1H, dd, $J = 13.8, 11.7, \alpha_1$-H), 4.07 (1H, dd, $J = 13.8, 3.0, \alpha_2$-H), 6.88 (2H, td, $J = 7.1, 1.2, 3''$-H + $7''$-H), 6.97 (2H, dd, $J = 8.0, 1.2, 1''$-H + $9''$-H), 7.12 (2H, ddd, $J = 8.0, 7.1, 1.3, 2''$-H + $8''$-H), 7.14 (2H, dd, $J = 7.1, 1.3, 4''$-H + $6''$-H), 7.73 (2H, m, $3'$-H + $5'$-H), 8.0 (2H, m, $2'$-H + $6'$-H); δ_C (150.8 MHz; +25 °C; $CDCl_3$; 20 mM) 21.7 (6-C), 22.2 (8-C), 25.1 (7-C), 51.6 (α-C), 116.3 ($1''$-C + $9''$-C), 121.5 ($2'$-C + $6'$-C), 122.0 ($3''$-C + $7''$-C), 125.3 ($4a''$-C + $5a''$-C), 125.9 ($4'$-C), 127.1 ($2''$-C + $8''$-C), 127.3 ($4''$-C + $6''$-C), 133.3 ($3'$-C + $5'$-C), 134.6 ($1'$-C), 146.2 ($9a''$-C + $10a''$-C), 162.4 (8a-C); δ_{10B} (64.4 MHz; +25 °C; $CDCl_3$; 20 mM) −11.3 (BH_2 br s); δ_C ($^{13}C\{^1H\}$-CP/MAS; 100.6 MHz; 7 kHz) 22.9, 26.4, 51.8, 116.7, 118.1, 121.0, 122.8, 124.2, 127.3, 129.0, 134.0, 144.0, 149.0, 163.1; $\delta_{11B,iso}$ ($^{11}B\{^1H\}$-MAS; 192.4 MHz; 11 kHz and $^{11}B\{^1H\}$-MAS; 128.3 MHz; 7 kHz) $\delta_{iso} = -12$ ppm ($Q_{cc} = 2.0$ MHz and $\eta = 0$); *m/z* (ESI+) $[M + Na]^+$: 514.0 ($C_{23}H_{21}BBrN_5S$ requires 490.23).

*3.2.2.3. 6-((10H-Phenothiazin-10-yl)methyl)-2-(4-methoxyphenyl)-5,6,7,8-tetrahydro-2H-tetrazolo[5,1-f][1,2]azaborinin-4-ium-5-uide (**4c**).* Starting from 10-((1*E*,3*E*)-4-(2-(4-methoxyphenyl)-2*H*-tetrazol-5-yl)buta-1,3-dien-1-yl)-10*H*-phenothiazine (**3c**, 0.425 g, 1 mmol) to give **4c** (0.096 g, 22%) as yellow-white crystals (mp 155–162 °C); (Found: N, 15.56; C, 65.17; H, 5.37; $C_{24}H_{24}BN_5OS$ requires N, 15.87; C, 65.31; H, 5.48%); ν_{max}(KBr)/cm^{-1} 3344, 2354, 1454, 1264 and 755; NMR data (+25 °C, $CDCl_3$, 30 mM): $\delta_{1H-\{11B\}}$ (399.9 MHz) 1.64 (1H, dddd, J = 13.0, 10.2, 9.8, 5.0, 7_{ax}-H), 1.74 (1H, br m, 6-H), 2.30 (1H, dddd, J = 13.0, 5.6, 5.0, 2.5, 7_e-H), 2.43 (1H, dd, J = 10.6, 5.9, BH_{ax}), 2.77 (1H, ddd, J = 17.7, 9.8, 5.6, 8_{ax}-H), 2.82 (1H, dd, J = 10.6, 4.0, BH_{eq}), 3.05 (1H, dt, J = 17.7, 5.0, 8_e-H), 3.71 (1H, dd, J = 14.2, 11.6, α_1-H), 3.91 (3H, s, 4′-OCH_3), 4.07 (1H, dd, J = 14.2, 3.1, α_2-H), 6.87 (2H, td, J = 7.5, 1.0, 3″-H + 7″-H), 6.99 (2H, dd, J = 7.9, 1.0, 1″-H + 9″-H), 7.04 (2H, m, 3′-H + 5′-H), 7.12 (2H, ddd, J = 7.9, 7.5, 1.5, 2″-H + 8″-H), 7.13 (2H, dd, J = 7.5, 1.5, 4″-H + 6″-H), 8.02 (2H, m, 2′-H + 6′-H); δ_C (100.6 MHz) 21.7 (6-C), 22.2 (8-C), 25.1 (7-C), 51.6 (α-C), 55.8 (4′-OCH_3), 115.0 (3′-C + 5′-C), 116.3 (1″-C + 9″-C), 121.7 (2′-C + 6′-C), 121.9 (3″-C + 7″-C), 125.3 (4a″-C + 5a″-C), 127.1 (2″-C + 8″-C), 127.3 (4″-C + 6″-C), 129.0 (1′-C), 146.2 (9a″-C + 10a″-C), 161.8 (8a-C), 161.9 (4′-C); δ_{10B} (43.0 MHz) −11.5 (br s, BH_2); $\delta_{C,iso}$ ($^{13}C\{^1H\}$-CP/MAS; 150.8 MHz; 10 kHz) 21.0, 23.9, 25.8, 51.6, 54.3, 61.9, 114.7, 116.0, 118.5, 119.7, 123.0, 126.2, 128.1, 145.0, 150.2, 162.2; m/z (ESI+) $[M + Na]^+$: 464.4, $[M + H]^+$: 442.3 ($C_{24}H_{24}BN_5OS$ requires 441.36).

*3.2.2.4. 6-((10H-Phenothiazin-10-yl)methyl)-2-(p-tolyl)-5,6,7,8-tetrahydro-2H-tetrazolo[5,1-f][1,2]azaborinin-4-ium-5-uide (**4d**).* Starting from 10-((1*E*,3*E*)-4-(2-(*p*-tolyl)-2*H*-tetrazol-5-yl)buta-1,3-dien-1-yl)-10*H*-phenothiazine (**3d**, 0.410 g, 1 mmol) to give **4d** (0.134 g, 32%) as yellow-white crystals (mp 167–172 °C); (Found: N, 16.19; C, 67.76; H, 5.70; $C_{24}H_{24}BN_5S$ requires N, 16.46; C, 67.77; H, 5.69%); ν_{max}(KBr)/cm^{-1} 3369, 2352, 1459, 1108 and 754; NMR data (+25 °C, $CDCl_3$, 30 mM): $\delta_{1H-\{11B\}}$ (399.9 MHz) 1.63 (1H, dddd, J = 12.0, 11.0, 10.0, 4.7, 7_{ax}-H), 1.73 (1H, br m, 6-H), 2.31 (1H, dddd, J = 12.0, 5.3, 5.0, 2.7, 7_e-H), 2.44 (1H, dd, J = 10.6, 5.3, BH_{ax}), 2.45 (3H, s, 4′-CH_3) 2.79 (1H, ddd, J = 17.7, 10.0, 5.3, 8_{ax}-H), 2.83 (1H, dd, J = 10.6, 3.9, BH_{eq}), 3.06 (1H, ddd, J = 17.7, 5.0, 4.7, 8_e-H), 3.71 (1H, dd, J = 14.1, 11.6, α_1-H), 4.07 (1H, dd, J = 14.1, 3.1, α_2-H), 6.87 (2H, td, J = 7.5, 1.0, 3″-H + 7″-H), 6.98 (2H, dd, J = 8.2, 1.0, 1″-H + 9″-H), 7.12 (2H, ddd, J = 8.2, 7.5, 1.5, 2″-H + 8″-H), 7.13 (2H, dd, J = 7.5, 1.5, 4″-H + 6″-H), 7.36 (2H, m, 3′-H + 5′-H), 7.97 (2H, m, 2′-H + 6′-H); δ_C (100.6 MHz) 21.3 (4′-CH_3) 21.7 (6-C), 22.2 (8-C), 25.1 (7-C), 51.6 (α-C), 116.3 (1″-C + 9″-C), 120.0 (2′-C + 6′-C), 121.9 (3″-C + 7″-C), 125.3 (4a″-C + 5a″-C), 127.1 (2″-C + 8″-C), 127.3 (4″-C + 6″-C), 130.5 (3′-C + 5′-C), 133.5 (1′-C), 142.2 (4′-C), 146.2 (9a″-C + 10a″-C), 161.9 (8a-C); δ_{10B} (43.0 MHz) −12.0 (br s, BH_2); $\delta_{C,iso}$ ($^{13}C\{^1H\}$-CP/MAS; 150.8 MHz; 10 kHz) 22.6, 26.5, 53.4, 117.1, 120.8, 124.7, 126.6, 127.9, 130.0, 133.6, 142.3, 144.3, 148.8, 162.3; m/z (ESI+) $[M + Na]^+$: 448.4, $[M + H]^+$: 426.2 ($C_{24}H_{24}BN_5S$ requires 425.36).

3.3. X-ray crystallography

X-ray structure: Crystal data: $C_{23}H_{21}BBrN_5S$, Fwt.: 490.23, yellow, block, size: 0.50 × 0.40 × 0.32 mm, monoclinic, space group $P2_1/n$ (No14), a = 12.547(2) Å, b = 9.8202(13) Å, c = 17.879(3) Å, $\alpha = \gamma = 90°$, β = 90.011(7)°, V = 2203.1(6) Å^3, T = 93(2) K, Z = 4, $F(000)$ = 1000, D_x = 1.478 Mg m^{-3}, μ = 1.98 mm^{-1}. A crystal of **4b** was mounted on a MiTeGen loop. Cell parameters were determined by least-squares of the setting angles of 77,979 ($3.08 \le \theta \le 27.49°$) reflections. Intensity data were collected on a Rigaku RAxis Rapid diffractometer (graphite monochromator; Mo-Kα radiation, λ = 0.71073 Å) at 93(2) K in the range $3.08 \le \theta \le 27.48°$ using dtprofit.ref scans. A total of 93,290 reflections were collected of which 5052 were unique [R_{int} = 0.0353, $R(\sigma)$ = 0.0123]; 4698 reflections were $I > 2\sigma(I)$. Completeness to 2θ = 0.998. A multi-scan absorption correction was applied to the data (the minimum and maximum transmission factors were 0.744 and 1.000). The structure was solved by direct methods (SHELXS-97) [12]. Neutral atomic scattering factors and anomalous scattering factors are taken from International Tables for X-ray Crystallography [13]. Anisotropic full-matrix least-squares refinement (SHELXL-97) [14,15] on F^2 for all non-hydrogen atoms yielded R1 = 0.0287 and wR2 = 0.0715 for 4698 [$I > 2\sigma(I)$] and R1 = 0.0315 and wR2 = 0.0731 for all (5052) intensity data (goodness-of-fit = 1.035 the maximum and mean shift/esd 0.001 and 0.000). Number of parameters = 284. The maximum and minimum residual electron density in the final difference map was 0.575 and −0.460 e Å^{-3}. The weighting scheme applied was

$$w = 1/\left[\sigma^2\left(F_o^2\right) + (0.0364P)^2 + 1.8626P\right] \quad \text{where}$$

$$P = \left(F_o^2 + 2F_c^2\right)/3$$

Hydrogen atomic positions were located in difference maps. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded.

Acknowledgments

The support of the OTKA 77784 and Hungarian GVOP-3.2.1.-2004-04-0210/3.0 projects as well as the National Science and Technology Office for an X-ray diffractometer purchase grant (MU-00338/2003) are gratefully acknowledged.

Appendix. Supplementary data

CCDC 757953 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.08.049.

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