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Mechanism of benzo-1,2,3,4-tetrazine 1-*N*-oxide formation

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Benzo-1,2,3,4-tetrazine 1-*N*-oxide formation involves the intramolecular cyclization of 2-(*tert*-butyl-*NNO*-azoxy)phenyldiazonium tetrafluoroborates and the N→N migration of the *tert*-butyl group to afford 2-(*tert*-butyl)benzo-1,2,3,4-tetrazinium 4-*N*-oxides 3 followed by elimination of the *tert*-butyl group. Compounds 3 were hydrolysed to give a new heterocyclic system, *viz*. 2-alkyl-6-oxo-2,6-dihydrobenzo-1,2,3,4-tetrazine 4-*N*-oxides. For 2-(*tert*-butyl)-8-bromo-6-oxo-2,6-dihydrobenzo-1,2,3,4-tetrazine 4-*N*-oxide an X-ray diffraction study was carried out.

Recently it was disclosed[1] that aryl diazonium salts with a *tert*-butylazoxy group in the *ortho*-position afford benzo-1,2,3,4-tetrazine 1-*N*-oxides, which arise from an intramolecular reaction. The present work was aimed at the investigation of the mechanism of this reaction.

Diazonium salts **1a**,**b** were prepared by the treatment of appropriate amines[2] with $NOBF_4$ at 0 °C. Their structure was confirmed by IR and NMR investigations.[1] In the solid state salts **1a**,**b** were rather stable at room temperature but in a short time cyclization occurred. In solution (acetonitrile, acetone) the reaction proceeded much faster. The cyclic structure of the new salts was established on the basis of the disappearance of the absorption band of the diazonium group (2270–2300 cm^{-1}) in the IR spectra. A downfield ^{13}C chemical shift of the tertiary carbon atom of the *tert*-butyl group (70 ppm) and its downfield ^1H chemical shift (2.0 ppm) in the NMR spectra also confirmed the cyclic structure.[†] However, these spectroscopic data alone did not allow us to choose between cyclic salts **2** and **3**.

In acetonitrile solutions containing H_2O, the elimination of the *tert*-butyl group from **3b** occurred to give benzo-1,2,3,4-tetrazine 1-*N*-oxide **5b** (quantitative yield based on ^1H NMR), *N*-*tert*-butyl acetamide (45% yield) and Bu^tOH (55% yield),[1] whereas in DMSO solutions containing water, nucleophilic displacement of the bromine atom took place to afford 2-(*tert*-butyl)-6-oxo-2,6-dihydro-benzo-1,2,3,4-tetrazine 4-*N*-oxides **4a**,**b**. NMR studies (^1H, ^{13}C, ^{14}N, ^{15}N NMR) have shown that these compounds feature a new heterocyclic system, and so an X-ray diffraction study for **4b** was undertaken (Figure 1).[‡]

All non-hydrogen atoms of molecule **4b** (Figure 1) with the exception of the C(11) and C(11a) atoms of the *tert*-butyl occupy special positions on the crystallographic mirror plane.

[†] NMR spectra were measured on a Bruker AM-300 spectrometer.

Spectral data for **1a** (in [$^2H_6$]acetone at 273 K): ^1H NMR δ 1.52 (9H, s, Bu^t), 8.52 (1H, dd, H-5), 8.86 (1H, d, $J = 2.0$ Hz, H-3), 8.87 (1H, d, $J = 8.6$ Hz, H-6); ^{13}C NMR δ 25.08 (Me), 62.03 (*C*Me), 109.67 (C-1), 130.20 (C-3), 137.40 (C-6), 137.84 (C-5), 138.30 (C-4), 146.70 (C-2); ^{14}N NMR δ −67 ($\Delta\nu_{1/2} = 100$ Hz, N→O), −151 ($\Delta\nu_{1/2} = 250$ Hz) (N_2^+).

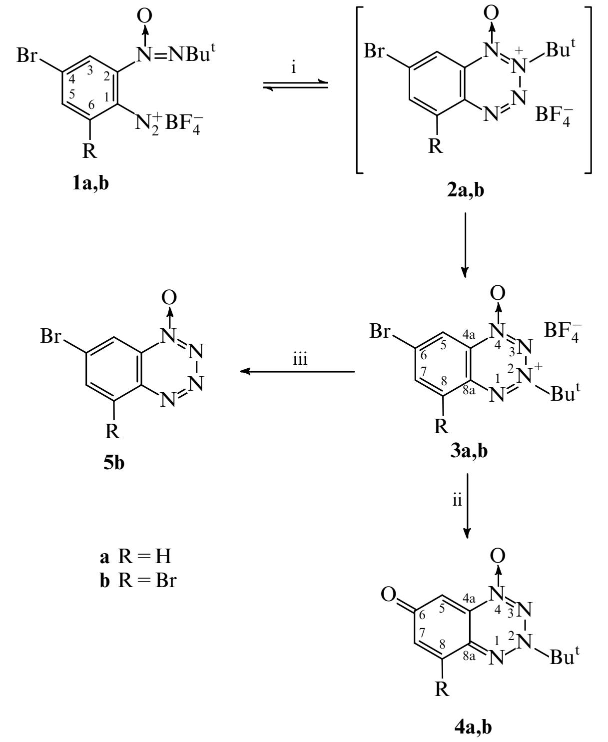
For **3a** (in [$^2H_6$]acetone at 278 K): ^1H NMR δ 2.05 (9H, s, Bu^t), 8.95 (1H, d, $^3J = 8.9$ Hz, H-8), 8.97 (1H, dd, H-7), 9.09 (1H, dd, $^4J = 1.6$, $^5J = 0.7$ Hz, H-5); ^{13}C NMR δ 28.85 (Me), 85.25 (*C*Me), 122.77 (C-5), 133.30 (C-8), 141.37 (C-6), 142.42 (C-8a), 146.06 (C-7); ^{14}N NMR δ −51 ($\Delta\nu_{1/2} = 70$ Hz); IR (KBr) ν_{max}/cm^{-1} 2290 (N_2^+).

For **4a**: ^1H, ^{14}N and ^{15}N NMR in [$^2H_6$]acetone; ^1H NMR δ 1.76 (9H, s, Bu^t), 6.65 (1H, d, $J = 2.3$ Hz, H-5), 7.05 (1H, dd, H-7), 7.74 (1H, d, $J = 9.7$ Hz, H-8); ^{13}C NMR (in [$^2H_6$]DMSO at 313 K) δ 28.20 (Me), 72.06 (*C*Me), 103.40 (C-5), 131.00 (C-8), 132.18 (C-4a), 134.50 (C-8a), 138.64 (C-7), 182.57 (C-6); ^{14}N NMR δ −77 ($\Delta\nu_{1/2} = 70$ Hz, N-4); ^{15}N NMR (INEPT) δ −127.6 (N-2); IR (KBr) ν_{max}/cm^{-1} 1620 (C=O).

For **4b**: ^1H and ^{14}N NMR in [$^2H_6$]acetone, ^{13}C and ^{15}N NMR in [$^2H_6$]DMSO; ^1H NMR δ 1.78 (9H, s, Bu^t), 6.64 (1H, d, $J = 2.3$ Hz, H-5), 7.42 (1H, d, H-7); ^{13}C NMR δ 28.22 (Me), 72.78 (*C*Me), 103.05 (C-5), 126.60 (C-8), 132.43 (C-8a), 133.80 (C-4a), 140.80 (C-7), 180.53 (C-6); ^{14}N NMR δ −74 ($\Delta\nu_{1/2} = 80$ Hz, N-4); ^{15}N NMR (INEPT) δ −40.8 (N-3), −60.3 (N-1), −74.6 (N-4), −127.0 (N-2); IR (KBr) ν_{max}/cm^{-1} 1605 (C=O).

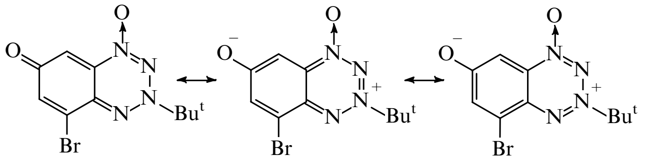
Compounds **4a**,**b** gave satisfactory elemental analyses and MS.

[‡] *Crystal data* for **4b**: $C_{10}H_{11}N_4O_2Br$, $M = 299.1$, orthorhombic, space group P_{nma}, at 293 K $a = 20.9259(3)$, $b = 6.638(2)$, $c = 8.556(2)$ Å, $V = 1188.4(8)$ Å^3, $Z = 4$, $d_{calc} = 1.672$ g cm^{-3}, $F(000) = 600$. The single-crystal X-ray diffraction study was carried out with a Siemens P3/PC diffractometer ($T = 293$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\theta/2\theta$ scan technique, $2\theta < 56°$). The structure was solved by direct methods and refined in the anisotropic approximation by the SHELXTL PLUS (PC Version) program.[3] Hydrogen atoms were included in calculated positions and refined in the riding model approximation with the common fixed $U_{iso} = 0.08$ Å^2. The empirical absorption correction [μ(MoKα) = 34.19 cm^{-1}] based on the azimuthal scans of 18 reflections was applied ($T_{min} = 0.460$). The final discrepancy factors are $R = 0.0658$, $R_w = 0.0668$ for 623 independent reflections with $I \geqslant 4\sigma(I)$. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details, see Notice to Authors, *Mendeleev Commun.*, 1996, issue 1.



Scheme 1 *Reagents and conditions:* i, for **a**: solid state, r.t., 7 days (68%); for **b**: solid state, 40 °C, 12 h (56%) or MeCN, r.t., 10 min (69%); ii, MeCN/20% DMSO/1% H_2O, 0 °C, 30 min, then neutralized with $NaHCO_3$ and chromatographed on SiO_2; **4a**, red crystals, mp 188–189 °C (decomp.), yield 27%, **4b**, red crystals, mp 168–169 °C (decomp.), yield 40%; iii, MeCN/2% H_2O, 10 °C, 1.5 h; **5b** isolated yield 70%, Bu^tOH yield 55% (based on ^1H NMR), $AcNHBu^t$ yield 45% (based on ^1H NMR).

The planar environment of the N(2) atom implies a considerable contribution of the **4b′** and **4b″** resonance forms although the relatively low accuracy of the structure would not justify a detailed analysis of bond length distribution.



4b **4b′** **4b″**

Taking into account the structural data for **4**, the cyclic salts were assigned the structure of **3** rather than of **2**. When the conversion **1a**→**3a** was monitored by *in situ* NMR, ring **2a** was not observed, hence the rearrangement **2**→**3** is probably a very fast process. It should be noted that such a type of rearrangement was not observed previously. *A priori* this N→N migration can be accommodated by an elimination–addition mechanism or by a simultaneous mechanism with a three-centre two-electron transition state. We suppose the latter is more probable because the rearrangement occurs in the solid state and the former mechanism needs an effective solvation. The driving force of this process should be the higher thermodynamic stability of **3** as compared to that of **2**.

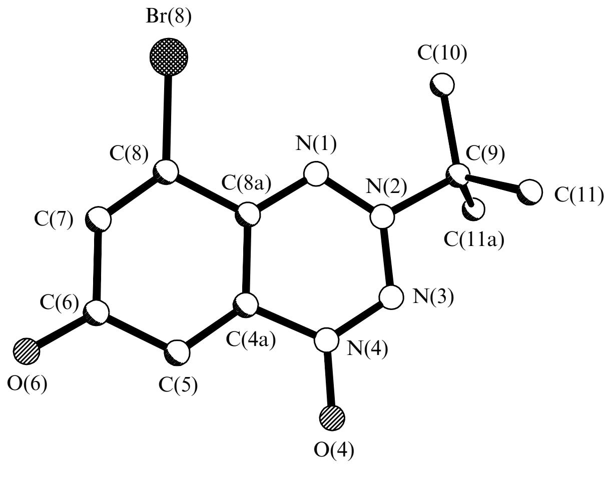


Figure 1 Molecular structure of **4b** (see Table 1).

Table 1 Selected bond lengths and bond angles in compound **4b**.

Bond	Bond length/Å	Angle	Bond angle/°
Br(8)–C(8)	1.87(2)	N(2)N(1)C(8a)	116.9(11)
N(2)–C(9)	1.52(2)	C(5)C(6)C(7)	115.6(17)
C(6)–C(7)	1.46(3)	N(1)N(2)N(3)	127.5(11)
O(4)–N(4)	1.26(2)	C(6)C(7)C(8)	127.3(15)
N(3)–N(4)	1.31(2)	N(1)N(2)C(9)	119.9(11)
C(7)–C(8)	1.32(2)	Br(8)C(8)C(7)	127.7(11)
O(6)–C(6)	1.21(2)	N(3)N(2)C(9)	112.6(11)
N(4)–C(4a)	1.44(2)	Br(8)C(8)C(8a)	115.4(10)
C(8)–C(8a)	1.49(2)	N(2)N(3)N(4)	116.5(11)
N(1)–N(2)	1.32(2)	C(7)C(8)C(8a)	116.9(14)
C(4a)–C(5)	1.34(2)	O(4)N(4)N(3)	118.5(12)
C(9)–C(10)	1.55(2)	N(1)C(8a)C(4a)	123.0(11)
N(1)–C(8a)	1.33(2)	O(4)N(4)C(4a)	117.1(12)
C(4a)–C(8a)	1.46(2)	N(1)C(8a)C(8)	121.9(13)
C(9)–C(11)	1.50(1)	N(3)N(4)C(4a)	124.4(12)
N(2)–N(3)	1.34(2)	C(4a)C(8a)C(8)	115.1(12)
C(5)–C(6)	1.42(2)	N(4)C(4a)C(5)	122.3(15)
		N(2)C(9)C(10)	109.0(10)
		N(4)C(4a)C(8a)	111.7(12)
		N(2)C(9)C(11)	107.2(8)
		C(5)C(4a)C(8a)	126.0(12)
		C(10)C(9)C(11)	111.1(8)
		C(4a)C(5)C(6)	119.0(17)
		O(6)C(6)C(5)	124.1(21)
		O(6)C(6)C(7)	120.3(16)

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