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Synthesis, Structure and Transformations of the First 1,2,3,4-Tetrazine-1-*N*-oxide

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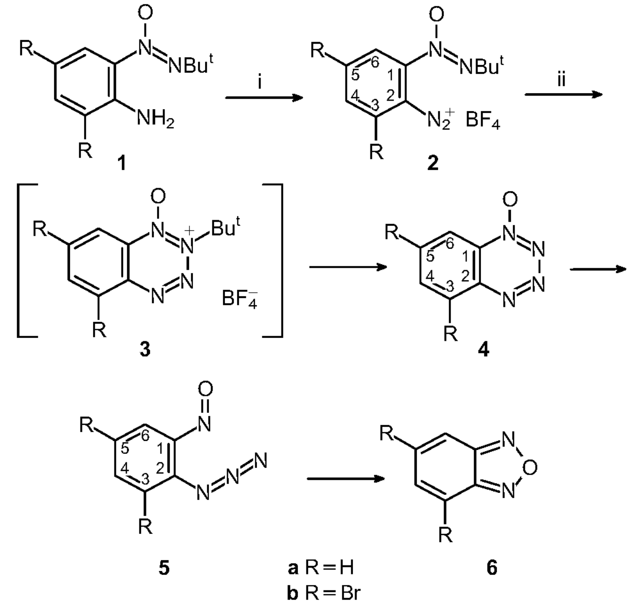
The first representative of the 1,2,3,4-tetrazine-*N*-oxides, 5,7-dibromobenzo-1,2,3,4-tetrazine-1-*N*-oxide **4b**, has been obtained by intramolecular reaction of *o*-(*tert*-butylazoxy)phenyldiazonium tetrafluoroborate **2b**. Compound **4b** has been characterized by NMR spectroscopy and an X-ray diffraction study and its transformation **4b** → **5b** → **6b** investigated; *o*-azidonitrosobenzene **5b** was isolated and characterized for the first time.

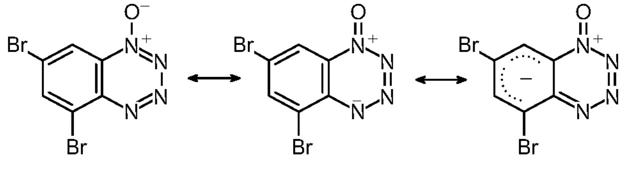
1,2,3,4-Tetrazine-1-*N*-oxides are formally derivatives of 1,2,3,4-tetrazine but they show essentially different chemical behaviour and therefore may be treated as a separate class of heterocycles. Thus, the only known 1,2,3,4-tetrazine, 2-phenyl-2*H*-[1,2,3]triazolo[4,5*e*][1,2,3,4]tetrazine **7**, is unstable at room temperature[1] whereas benzo-1,2,3,4-tetrazine-1,3-di-*N*-oxide (BTDO) is a quite stable compound with m.p. 170–172 °C. Thus, it seemed worthwhile to prepare the mono-*N*-oxide of benzo-1,2,3,4-tetrazine (BTO) and study its properties.

The traditional route to heterocyclic *N*-oxides involving the oxidation of the corresponding azines is impractical in our case because the parent benzo-1,2,3,4-tetrazine is not known. We planned to obtain BTO by intramolecular reaction of *o*-(*tert*-butylazoxy)phenyldiazonium tetrafluoroborate **2**. This salt might form a cyclic cation **3**, which could eliminate the *tert*-butyl cation (Scheme 1). This method is similar to that used by us to obtain BTDO.[2]

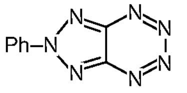
Diazonium tetrafluoroborate **2a**, which was prepared by diazotization of aniline **1a**, proved to be rather stable and did not react in solution at room temperature. It was characterized by IR and NMR spectroscopy.[†] As the temperature increased the reaction took place, but it was impossible to isolate BTO **4a**. The only reaction product was benzofurazan **6a**. The diazonium salt **2b** obtained from dibromoaniline **1b** proved to be more reactive and yielded BTO **4b** along with the product of



Scheme 1 *Reagents and conditions*: i, NOBF$_4$, MeCN, $-10 \rightarrow 0$ °C (**2a** 94%; **2b** 78%); ii, for **6a** and **6b**: MeCN, 50 °C, 1 h, (~90%); for **4b** (81%) and **5b** (11%) see below.[§]



4b **4b′** **4b″**



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its further transformation **5b** at room temperature. BTO **4b** was isolated in its pure state; it decomposes slowly at room temperature but can be stored in refrigerator for a long time. We performed NMR spectroscopic† and X-ray investigations‡ on it.

The molecule **4b** (Fig. 1) is almost planar: the deviations of atoms from the mean plane do not exceed 0.045 A. The distinctive feature of this compound as compared with tetrazine **7** is the uniformity of the N(1)–N(2) and N(2)–N(3) bond length [1.34(1) and 1.35(1) A, respectively]. The relevant bond lengths in tetrazine **7** are noticeably different (1.31 and 1.39 A, respectively[5]). This distinction can be attributed to the electron-releasing effect of the *N*-oxide oxygen atom, which is the reason for redistribution of π-electron density in the molecule reflecting a considerable contribution of the **4b′** resonance form.

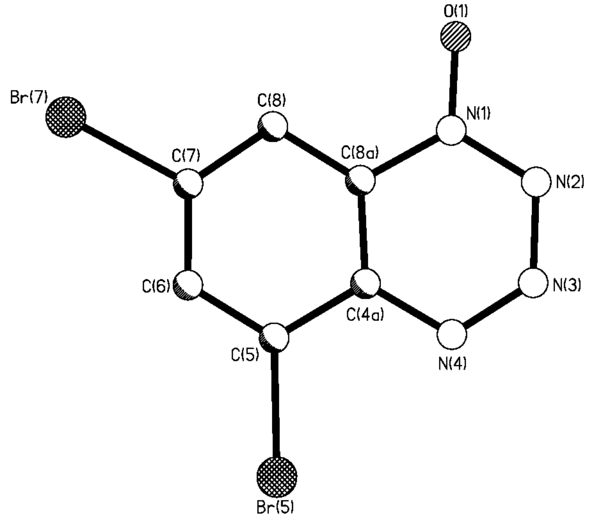

Fig. 1 Molecular structure of **4b**. Selected bond lengths (A): Br(5)–C(5) 1.88(1), Br(7)–C(7) 1.90(1), O(1)–N(1) 1.24(1), N(1)–N(2) 1.34(1), N(1)–C(8a) 1.41(1), N(2)–N(3) 1.35(1), N(3)–N(4) 1.30(1), N(4)–C(4a) 1.36(1), C(5)–C(6) 1.38(2), C(5)–C(4a) 1.43(2), C(6)–C(7) 1.37(1), C(7)–C(8) 1.38(1), C(8)–C(8a) 1.38(1), C(4a)–C(8a) 1.40(1). Bond angles (°): N(2)N(1)C(8a) 121(1), N(1)N(2)N(3) 119(1), N(2)N(3)N(4) 124(1), N(3)N(4)C(4a) 118(1), C(6)C(5)C(4a) 120(1), C(5)C(6)C(7) 120(1), C(6)C(7)C(8) 124(1), C(7)C(8)C(8a) 116(1), N(4)C(4a)C(8a) 123(1), C(5)C(4a)C(8a) 117(1), N(1)C(8a)C(4a) 115(1), C(8)C(8a)C(4a) 124(1).

The elongation of the C(8a)–N(1) [1.41(1) A] as compared to the C(4a)–N(4) bond [1.36(1) A] may be explained by contribution of the **4b″** form. The bond length inequality brings about considerable deviations of bond angles at C(4a) and C(8a) atoms from the ideal value of 120° (Fig. 1).

As expected, the chemical properties of 1,2,3,4-tetrazine-1-*N*-oxides are distinctly different from those of 1,2,3,4-tetrazines[1] and 1,2,3,4-tetrazine-1,3-di-*N*-oxides.[2] Thus, the only method of BTO decomposition is opening of the tetrazine ring to give an open-chain tautomer, *o*-azidonitrosobenzene **5**, which in its turn eliminates the N_2 molecule yielding benzofurazan **6**. However, the same reaction pathway is neither possible for 1,2,3,4-tetrazines nor for BTDO. The transformations **4b** → **5b** → **6b** were monitored by *in situ* NMR spectroscopy.

It should be noted that *o*-azidonitrosobenzene **5b** is the first isolated compound of this type. Previously, *o*-azidonitrosobenzenes had been suggested as intermediates in benzofurazan synthesis,[6] which was confirmed by IR spectroscopy, but the conditions of the reaction were too rigorous to isolate them. In our case it was possible to isolate **5b** in no less than 95% purity as a yellow solid and characterize it by IR and NMR† spectroscopy. According to ^{1}H and ^{13}C NMR data it does not form a dimer even at −25 °C. Its solutions are yellow, rather than green, which is probably due to the strong conjugation between azido and nitroso groups.

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† NMR spectra were measured on a Bruker AM-300 spectrometer in $[^{2}H_6]$acetone.

Spectral data for **2a**: ^{1}H NMR (300 MHz, standard TMS) δ 1.53 (s, 9H, Bu^{t}), 8.25 (t, 1H, 4-H, ^{3}J 8.2 Hz), 8.52 (t, 1H, 5-H, ^{3}J 8.2 Hz), 8.70 (d, 1H, 6-H, ^{3}J 8.2 Hz), 8.99 (d, 1H, 3-H, ^{3}J 8.2 Hz); ^{13}C NMR δ 25.35 (Me), 61.93 (*C*Me), 110.93 (C-2), 127.05 (C-6), 134.80 (C-4), 137.12 (C-3), 143.07 (C-5), 146.65 (C-1); ^{14}N NMR (δ, standard $MeNO_2$) −66.3 ± 2 ($\Delta\nu_{0.5}$ = 85 Hz) (N→O), −153.6 ± 3 ($\Delta\nu_{0.5}$ = 240 Hz) ($N^{+}\equiv N$); ^{15}N NMR (INEPT, δ, standard $MeNO_2$) −6.91 (=N–Bu^{t}); IR (KBr) ν_{max}/cm^{-1} 2300 (N_2^{+}).

For **4b**: m.p. 78–80 °C (decomp.); ^{1}H NMR, δ 8.66 (d, 1H, 6-H, ^{4}J 1.8 Hz), 8.87 (d, 1H, 4-H); ^{13}C NMR δ 121.00 (C-6, ^{1}J 180.8, ^{3}J 5.4 Hz), 125.42 (C-3, ^{2}J 4.5, ^{4}J 1.7 Hz); 131.22 (C-5, ^{2}J 4.0 Hz), 132.70 (C-1, br.), 140.43 (C-2, ^{3}J 7.4, ^{3}J 4.9 Hz), 144.11 (C-4, ^{1}J 177.0, ^{3}J 6.5 Hz); ^{14}N NMR (δ, standard $MeNO_2$) −51.7 ± 1 ($\Delta\nu_{0.5}$ = 50 Hz) (N→O).

For **5b**: ^{1}H NMR, δ 6.23 (d, 1H, 6-H, ^{4}J 2.1 Hz), 8.20 (d, 1H, 4-H); ^{13}C NMR δ 110.10 (C-6), 118.50 (C-5), 119.20 (C-3), 143.05 (C-4), 145.40 (C-2), 159.02 (C-1); ^{14}N NMR (δ, standard $MeNO_2$) −143.1 ± 1 ($\Delta\nu_{0.5}$ = 100 Hz) (N_3). IR (KBr) ν_{max}/cm^{-1} 2120, 2150 w (N_3).

‡ *Crystal data* for **4b**: $C_6H_2Br_4N_4O_2$, $M = 305.9$, orthorhombic, space group $P2_12_12_1$, at 154 K, $a = 5.201(2)$, $b = 8.255(2)$, $c = 19.555(4)$ A, $U = 839.5(3)$ A^3, $Z = 4$, $D_{calc} = 2.421$ g cm^{-3}. Cell dimensions and intensities of 1715 unique reflections were measured with a Siemens P3/PC diffractometer (154 K, graphite monochromated MoKα radiation, $\lambda = 0.71073$ A, θ/2θ scan technique, $2\theta > 64°$).The structure was solved by direct methods and refined by the least-squares technique in the anisotropic approximation. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the riding motion approximation with common refined $U_{iso} = 0.07(3)$ A^2. The final discrepancy factors are $R = 0.0442$ ($R_w = 0.0497$) for 914 reflections with $I \geqslant 3\sigma(I)$. The absorption correction ($\mu = 96.2$ cm^{-1}) by means of the DIFABS[3] program was applied. The absolute structure was determined on the basis of the Hamilton test at the 99.5% probability level (R- and R_w-factors for the inverted structure are 0.0537 and 0.0603, respectively). All calculations were carried out on an IBM PC using SHELXTL PLUS (PC Version).[4] Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre; see Notice to Authors, *Mendeleev Commun.*, Issue 1, 1994.

§ *Experimental*: Salt **2b** was placed on a small quantity of silica gel and eluted with warm $CHCl_3$ (40 °C). The solution was collected in a well-cooled flask, then solvent was removed under reduced pressure at 0 °C. The residue contained **4b** and **5b**, and was washed with pentane to give pure **4b** as a yellow solid (81%). The evaporation of pentane extract under reduced pressure (0 °C) gave **5b** as a yellow solid (11%).

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