First Synthesis of a 1,2,3,4-Tetrazine

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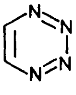
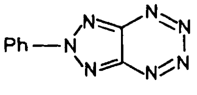
6-Phenyl[1,2,3]triazolo[4,5-*e*]-1,2,3,4-tetrazine (**2**), the first example of an aromatic 1,2,3,4-tetrazine, has been synthesized and its structure determined by *X*-ray crystallography.

The oxidation of 1-aminobenzotriazole is a convenient method for generation of the benzyne intermediate. The reported reaction mechanism suggested the presence of a 1,2,3,4-tetrazine ring as a precursor of benzyne.[1] 1,2,3,4-Tetrazine (**1**) is a basic aza-aromatic system, but one that has never been synthesized.[2] We report here the first example of a 1,2,3,4-tetrazine, compound (**2**), which was synthesized by the oxidation of the triazolotriazole (**3**).†

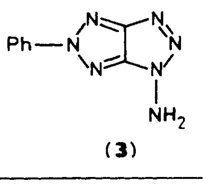
Compound (**3**) was oxidized‡ by lead tetra-acetate in methylene chloride at 0 °C, and careful work-up gave reddish crystals [m.p. 76—77 °C (decomp.) from CH_2Cl_2, explosive on heating or impact, ^1H n.m.r. (CD_2Cl_2) δ 7.68—7.85 (3H, m), 8.63—8.80 (2H, m); ^{13}C n.m.r. (CD_2Cl_2) δ 122.9 (d), 130.8 (d), 134.2 (d), 139.0 (s), 145.7 (s); ν_{max} (KBr) 3075, 1578, 1552, 1482, and 1458 cm^{-1}] in 81% yield. This compound decomposed in CH_2Cl_2 at room temperature accompanied by N_2 evolution to give the cyanotetrazole (**4**)[3] and the triazole (**5**).[4] The ^1H and ^{13}C n.m.r. spectra at −20 °C showed that the foregoing reddish compound has five phenyl protons, together with a non-phenyl carbon atom.



(**1**)



(**2**)



(**3**)

These facts implied that this compound was the triazolotetrazine (**2**). However, it was impossible to carry out elemental analyses or mass spectroscopic measurements because of the instability of the reddish product.

The structure of (**2**) was finally established by *X*-ray

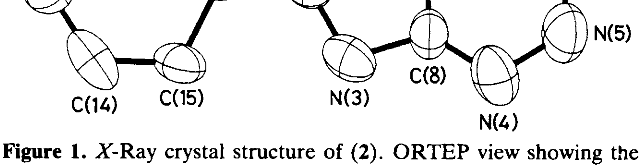


Figure 1. *X*-Ray crystal structure of (**2**). ORTEP view showing the atom numbering figure. Important parameters: N(1)–N(2) 1.359, N(2)–N(3) 1.299, N(2)–C(10) 1.476, N(3)–C(8) 1.351, N(1)–C(9) 1.328, C(8)–C(9) 1.444, C(9)–N(7) 1.348, N(7)–N(6) 1.308, N(6)–N(5) 1.405, C(8)–N(4) 1.268, N(5)–N(4) 1.325 Å; C(8)–C(9)–N(7) 118.57, C(9)–N(7)–N(6) 118.66, N(7)–N(6)–N(5) 119.87, N(6)–N(5)–N(4) 122.60, N(5)–N(4)–C(8) 117.51, N(4)–C(8)–C(9) 122.47 °.

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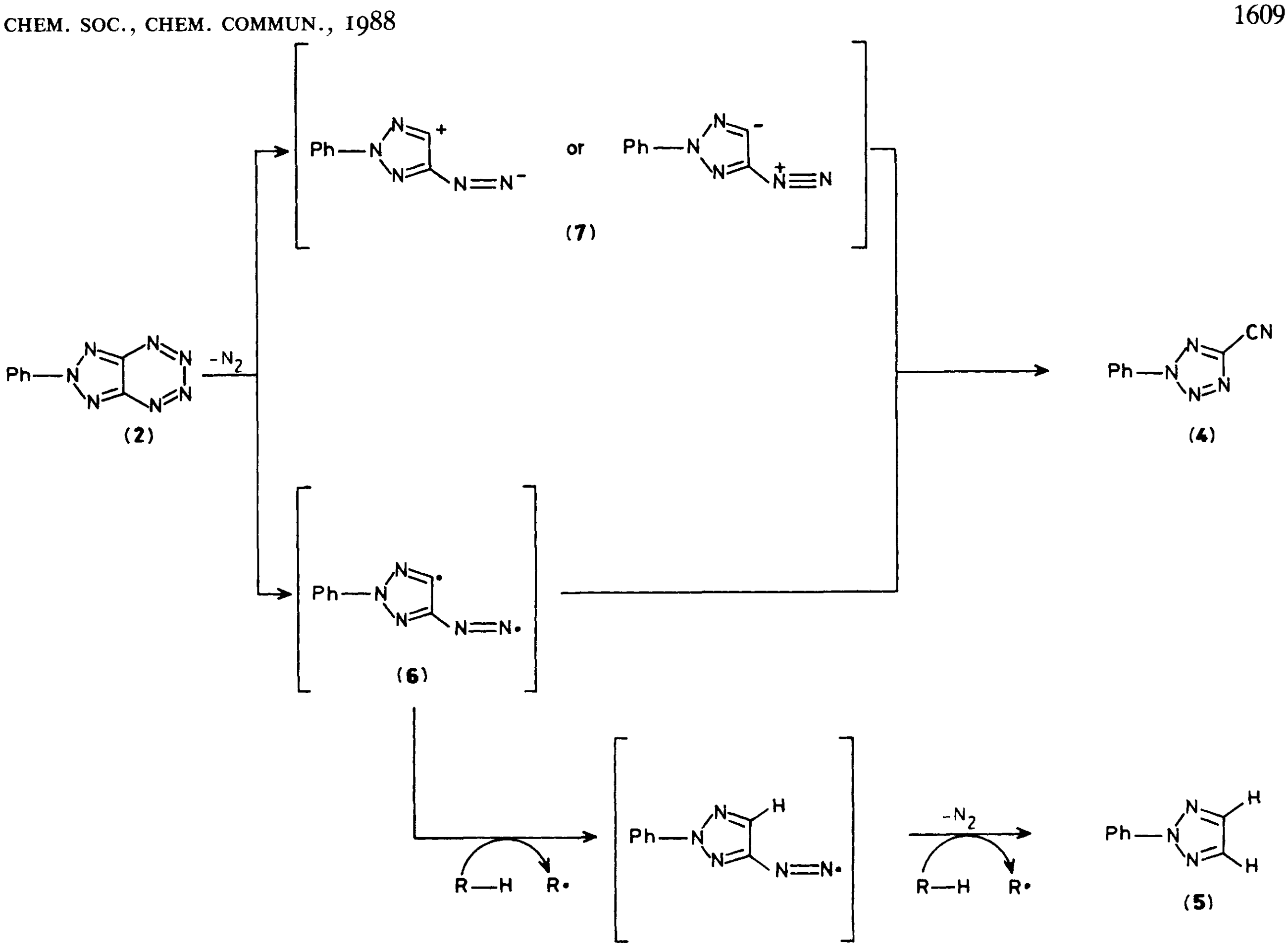
† Compound (**3**) was obtained along with the 2-amino isomer by amination of 5-phenyl[1,2,3]triazolo[4,5-*d*]-1,2,3-triazole[6] with (*O*-mesitylenesulphonyl)hydroxylamine.[7]

‡ A similar method was used for the synthesis of 1,2,3-triazines by oxidation of *N*-aminopyrazoles.[8]



Scheme 1

crystallography.§ Figure 1 shows an ORTEP drawing. The tetrazine ring of (**2**) is essentially planar,¶ and its bond lengths and bond angles supported its aromaticity.

The formation of (**4**) and (**5**) also suggested the presence of (**2**) in solution. Thus, the tetrazine (**2**) in solution was denitrogenated to form the biradical (**6**) or the zwitterion (**7**), which isomerized to the tetrazole (**4**). Hydrogen extraction of the biradical (**6**) from the solvent, followed by denitrogenation and hydrogen abstraction from the solvent gave the triazole (**5**) (Scheme 1).

The physical and chemical data obtained for this compound thus are consistent with structure (**2**). The stability of the parent 1,2,3,4-tetrazine has been discussed on the basis of M.O. calculations.[5] In this work, we have shown that the 1,2,3,4-tetrazine ring is able to exist, at least in ring-fused form. We think that the stability of our tetrazine is due to stabilisation with respect to nitrogen elimination of an intermediate nitrene, which causes ring expansion to the tetrazine.

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§ *Crystal data*: $C_8H_5N_7$, reddish flake ($0.35 \times 0.45 \times 0.02$ mm^3), $M = 199.2$, monoclinic, space group $P2_1/a$, $a = 17.651(34)$, $b = 5.362(7)$, $c = 10.860(23)$ Å, $\beta = 122.31(13)°$, $V = 868.7(3.0)$ Å^3, $D_c = 1.523$ g cm^{-3}, $Z = 4$. 1459 Diffraction data were collected with graphite monochromated Cu-$K_{\alpha1}$ radiation ($\lambda = 1.54050$ Å), on Rigaku AFC-5 four-circle diffractometer. 1205 reflections [$I>\sigma(I)$] with $2\theta \leqslant 120°$ were used in the refinement. Lorentz and polarization corrections were applied. Data were corrected for decay using standard reflections. The structure was solved by direct methods and refined by full-matrix least-squares. The final R value using anisotropic temperature factors for non-hydrogen atoms was 0.168 (R_w 0.146). The high R value was due to crystal instability; the intensities of standard reflections decayed by 15.1% during data collection. However, the standard deviations of bond lengths and angles are sufficiently low to provide a satisfactory basis for discussion ($\sigma_{\text{length}} = 0.015$ Å, $\sigma_{\text{angle}} = 0.84°$). The maximum residual peak height in the final difference fourier synthesis was 0.8e/Å^3. The atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

¶ The distance from the least-square plane calculated from the 6-membered ring atoms (N-4, N-5, N-6, N-7, C-8, C-9) ranged from −0.018 Å to 0.016 Å.

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