Benzo-*as*-triazine Tri-*N*-oxide; a Novel Cycloaddition Product from Reactions of Benzofurazan *N*-Oxides with Nitrile Oxides

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Benzo-*as*-triazine tri-*N*-oxides have been formed from the reaction of nitrile oxides with benzofurazan *N*-oxides and the structure of one derivative has been confirmed by an *X*-ray crystal structure analysis.

We report the first synthesis and crystal structure of a triazine *N*-oxide. Although triazines and benzotriazines have been widely studied,[1] until now their tri-*N*-oxides were unknown. Our interest in furoxans[2] led to the discovery that these tri-*N*-oxides can be prepared from the reaction of benzofurazan *N*-oxides with nitrile oxides.

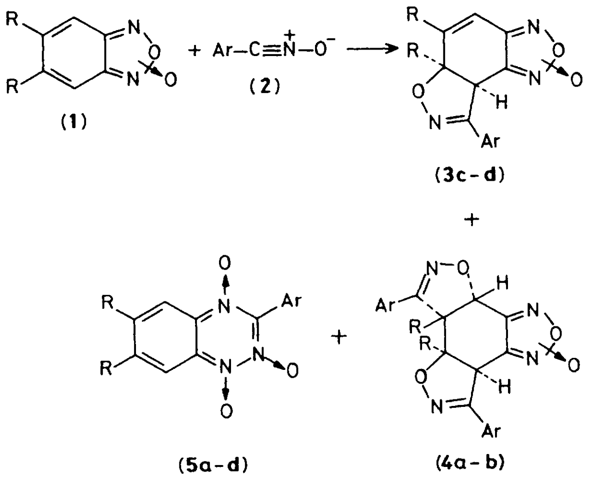
Despite intensive work on benzofurazan *N*-oxides (**1**),[3] there are only a few studies involving their reactions with 1,3-dipoles or dienes.[4] We find that they react with nitrile oxides (**2**) to give the expected addition products (**3**) and (**4**). However, in all cases, a deep yellow, thermally stable product is also formed which has been characterized as the tri-*N*-oxide (**5**). A typical reaction involves refluxing a mixture of benzofurazan N-oxide (**1**) (2 mmol) and nitrile oxide (**2**) (4 mmol) in dichloromethane. The reaction mixture is chromatographed on silica gel using hexane–ethyl acetate (5 : 1) as the eluant. Compound (**3**) is eluted first followed by (**4**). The yellow tri-*N*-oxide (**5**) is eluted with ethyl acetate. The compounds isolated are given in Table 1.

Structural assignments were made on the basis of spectral data (i.r., m.s., ^{1}H and ^{13}C n.m.r.). The regiochemistry of (**3**) and (**4**) was deduced from the n.m.r. spectra, and their mass spectra gave the parent ion and the expected fragmentation

Table 1. Reactions of benzofurazan *N*-oxides (**1**) with nitrile oxides (**2**).

R[a]	Ar	Product[b]	Yield/%	M.p./°C
H	2,4,6-$Me_3C_6H_2$	(**4a**)	40	210—220
H	2,6,-$Cl_2C_6H_3$	(**4b**)	46	235 (decomp.)
Me	2,4,6-$Me_3C_6H_2$	(**3c**)	42	140—145
Me	2,6-$Cl_2C_6H_3$	(**3d**)	40	167—170
H	2,4,6-$Me_3C_6H_2$	(**5a**)	12	210—212
H	2,6-$Cl_2C_6H_3$	(**5b**)	3	205—207
Me	2,4,6-$Me_3C_6H_2$	(**5c**)	7	195—197 (decomp.)
Me	2,6-$Cl_2C_6H_3$	(**5d**)	6	194—195

[a] In the cases of R = H no mono-adducts (**3**) were isolated. When R = Me the bis-adducts (**4**) are formed in traces. [b] All compounds gave satisfactory elemental analyses (C,H,N).



a; R = H, Ar = 2,4,6-$Me_3C_6H_2$
b; R = H, Ar = 2,6-$Cl_2C_6H_3$
c; R = Me, Ar = 2,4,6-$Me_3C_6H_2$
d; R = Me, Ar = 2,6-$Cl_2C_6H_3$

Scheme 1

pattern. More details on the structure, reactions, and isomerizations of (**3**) and (**4**) will be given elsewhere.

The mass spectra of the tri-*N*-oxides (**5**) gave the parent ion followed by the consecutive loss of three oxygen atoms, typical of an *N*-oxide. The n.m.r. spectra were consistent with a tri-*N*-oxide, and an *X*-ray structural investigation was undertaken on (**5c**) (Figure 1).†

Both the triazine and mesityl groups are planar. The angle between the two groups is 104°, minimizing steric interactions. The N–O distances of 1.251(3) Å for both N(1)–O(1) and N(2)–O(2) are at the lower range of N–O distances (1.260—1.341 Å) found in other non-protonated *N*-oxides‡ and in a reported di-*N*-oxide (1.294 and 1.308 Å).[5] The remaining distances and angles have the expected values.

The formation of the tri-*N*-oxides (**5**) is unusual, although the reaction is analogous to the Beirut reaction.[3] It appears to be a [4 + 2] reaction where the nitrile oxide contributes two electrons and the benzofurazan *N*-oxide contributes four electrons. However, there is no evidence as to the actual reaction mechanism.

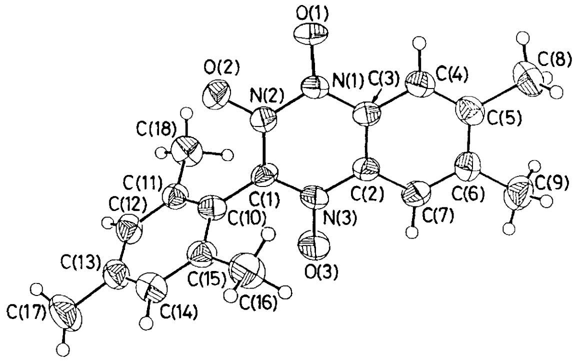


Figure 1. A view of the mesitylbenzotriazine tri-*N*-oxide (**5c**) showing the atomic numbering and thermal ellipsoids. Selected distances are: N(1)–O(1), 1.251(3); N(2)–O(2), 1.251(3); N(3)–O(3), 1.279(4); N(1)–N(2), 1.379(3); N(2)–C(1), 1.371(4); C(1)–N(3), 1.337(4); C(1)–C(10), 1.460(4); N(3)–C(2), 1.397(4) Å. Pertinent angles: N(2)–N(1)–C(3), 118.7(2); N(1)–N(2)–C(1), 121.3(2); N(2)–C(1)–N(3), 119.7(3); C(1)–N(3)–C(2), 121.1(3)°.

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† *Crystal data*: $C_{18}H_{19}N_3O_3$, $M = 325.37$, monoclinic, space group $P2_1/n$, $a = 8.722(4)$, $b = 11.194(6)$, $c = 16.691(7)$ Å, $\beta = 90.12(4)°$, $U = 1630(1)$ Å^3, $D_c = 1.33$ g cm^{-3}, $F(000) = 688$, $\mu(\text{Mo-}K_\alpha) = 0.85$ cm^{-1}, Nicolet R3m diffractometer, 2154 reflections ($1.0 \leqslant 2\theta \leqslant 45.0°$), 1158 observed with $F_o > 6.0\,\sigma(F_o)$. The structure was solved by direct methods (SOLV in the SHELXTL, system) and refined using the 'blocked cascade' least-squares method. The final R and R_w ($w = 1/\sigma^2$) values are 0.037 and 0.043 respectively; G.O.F. = 0.828. 293 Parameters refined: co-ordinates of all atoms, anisotropic thermal parameters of the non-H atoms, an isotropic thermal parameter for the H atoms, and a scale factor. Least-squares refinement was also carried out with and without varying the hydrogen parameters and with both $F_o > 5\sigma(F_o)$ and $F_o > 6\sigma(F_o)$. There were no significant differences in the bond distances and angles in the four cases. Full details and further discussion of the various refinements will be presented elsewhere. 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.

‡ A search of the 1988 release of the Cambridge Structural Database produced 32 examples of simple unco-ordinated and unprotonated aryl *N*-oxides. Further details will be given elsewhere.