

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

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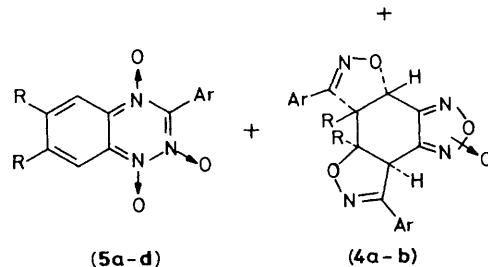
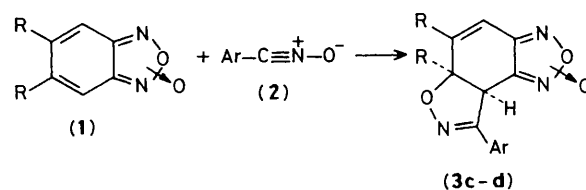
Benzo-*as*-triazine tri-*N*-oxides have been formed from the reaction of nitrile oxides with benzofurazan *N*-oxides and the structure of one derivative has been confirmed by an X-ray crystal structure analysis.

We report the first synthesis and crystal structure of a triazine *N*-oxide. Although triazines and benzotriazines have been widely studied,<sup>1</sup> until now their tri-*N*-oxides were unknown. Our interest in furoxans<sup>2</sup> 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),<sup>3</sup> there are only a few studies involving their reactions with 1,3-dipoles or dienes.<sup>4</sup> 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 chromatog-

raphed 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., <sup>1</sup>H and <sup>13</sup>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



a: R = H, Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>  
 b: R = H, Ar = 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  
 c: R = Me, Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>  
 d: R = Me, Ar = 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

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

R <sup>a</sup>	Ar	Product <sup>b</sup>	Yield/%	M.p./°C
H	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	(4a)	40	210–220
H	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	(4b)	46	235 (decomp.)
Me	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	(3c)	42	140–145
Me	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	(3d)	40	167–170
H	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	(5a)	12	210–212
H	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	(5b)	3	205–207
Me	2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	(5c)	7	195–197 (decomp.)
Me	2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	(5d)	6	194–195

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

Scheme 1

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

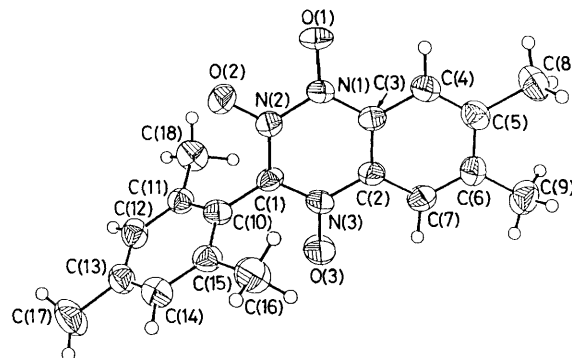
The mass spectra of the tri-*N*-oxides (5) gave the parent ion followed by the consecutive loss of three oxygen atoms, typical of an *N*-oxide. The n.m.r. spectra were consistent with a tri-*N*-oxide, and an *X*-ray structural investigation was undertaken on (5c) (Figure 1).†

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).<sup>5</sup> 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.<sup>3</sup> 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.

† *Crystal data*: C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>, *M* = 325.37, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 8.722(4), *b* = 11.194(6), *c* = 16.691(7) Å, β = 90.12(4)°, *U* = 1630(1) Å<sup>3</sup>, *D*<sub>c</sub> = 1.33 g cm<sup>-3</sup>, *F*(000) = 688, μ(Mo-*K*<sub>α</sub>) = 0.85 cm<sup>-1</sup>, Nicolet R3m diffractometer, 2154 reflections (1.0 ≤ 2θ ≤ 45.0°), 1158 observed with *F*<sub>o</sub> > 6.0 σ(*F*<sub>o</sub>). 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*<sub>w</sub> (*w* = 1/σ<sup>2</sup>) 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*<sub>o</sub> > 5σ(*F*<sub>o</sub>) and *F*<sub>o</sub> > 6σ(*F*<sub>o</sub>). 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.



**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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