1,2-Dinitrosobenzene in Argon Matrices at 14 K

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Photolysis of benzofurazan 1-oxide 3 and 2-nitrophenyl azide 7 in Ar matrices at 14 K yielded 1,2-dinitrosobenzene 4, which had not previously been characterized; the IR and UV absorptions of matrix-isolated 4 have been recorded, and its thermal and photochemical reversion to 3 has also been observed, ¹⁵N labelling experiments lend strong support to the assignment.

Thermal and photochemical rearrangements of a number of substituted benzofurazan 1-oxides, e.g. 1a–f and 2a–f, have previously been observed.[1–3] Likely intermediates in these rearrangements are the corresponding 1,2-dinitrosobenzenes, but so far there has been no direct evidence for these elusive species.

In this paper we report the results of matrix isolation studies of the photochemistry of the parent benzofurazan 1-oxide 3 and of 2-nitrophenyl azide 7. In both cases, 1,2-dinitrosobenzene is formed, and is stable enough in Ar at 14 K for its IR and UV–visible spectra to be recorded.

Benzofurazan 1-oxide 3[4] was sublimed at room temperature into a stream of Ar, and the resulting vapour was condensed on a CsI window at 14 K.[5] The IR absorptions of the resulting matrix are given in Table 1 and compare closely with those of the Nujol mull spectrum of 3. Near–UV irradiation of the resulting matrix (λ 365 ± 5 nm) led to the diminution of the intensity of the IR bands of 3 and concomitant growth of a set of new bands, the strongest of which appeared at 1516 cm⁻¹. Because the band at 1516 cm⁻¹ corresponds very closely with the expected v(N=O) band of dinitrosobenzene 4,† the new IR bands are assigned to this species (Table 1), and this is supported by ¹⁵N-labelling (see below).

A similar experiment, carried out with less material on the cold window, allowed the reaction to be followed by UV–visible spectroscopy. Compound 3 showed a strong absorption with λ_{max} at 360 nm (Fig. 1a). This diminished in intensity on UV irradiation of the matrix (λ 365 ± 5 nm), while a new, weaker, but clearly structured absorption appeared in the region 300–350 nm (Fig. 1b). On further irradiation with λ 320 ± 5 nm, partial regeneration of 3 occurred (Fig. 1c). The weak structured absorption at 300–350 nm is therefore also

assigned to 4. Once the UV absorption of 4 was determined, it was also possible to demonstrate in the matrix-IR spectrum the same photoreversal of 4 to 3 brought about by light of λ 320 ± 5 nm. Thus, on 360 nm irradiation, IR bands due to 3 diminished and those due to 4 grew, while on 320 nm irradiation, the reverse was observed. In addition to these photochemical interconversions of 3 and 4, the thermal reversal of 4 to 3 was also observed in the UV–visible spectrum when an Ar matrix containing 4 was warmed slowly to 90 K. During this process the Ar evaporated, but the sample retained sufficient optical clarity to allow the progressive growth in the 360 nm absorption of 3 to be seen. The reaction began to occur at a temperature as low as 35–40 K.

The matrix photoproduct of 3 was identified as 4 on the following basis. It could be interconverted with 3 by narrow-band photolysis, thus suggesting that it is an isomer of 3. It has an IR band corresponding exactly in frequency with that expected for a nitroso compound. Alternative structures, e.g. 5 (strongest band expected at ca. 1400 cm⁻¹)[6] and 6 (no strong band expected at ca. 1516 cm⁻¹), do not fit the spectroscopic data. The thermal reversal of the photoproduct to 3 would not be expected to occur at temperatures as low as 35–40 K, if an energy barrier due to bond-breaking had to be overcome, as would be needed for 5 or 6. On the other hand, the stability of 4 in Ar matrices may be due merely to formation of the anti conformer (as shown) and its inability to undergo internal rotation about one of the C–N bonds back to the reactive amphi conformer. Photon absorption by anti-4 or simply warming to temperatures above 40 K would supply the necessary energy to effect this conformational change.
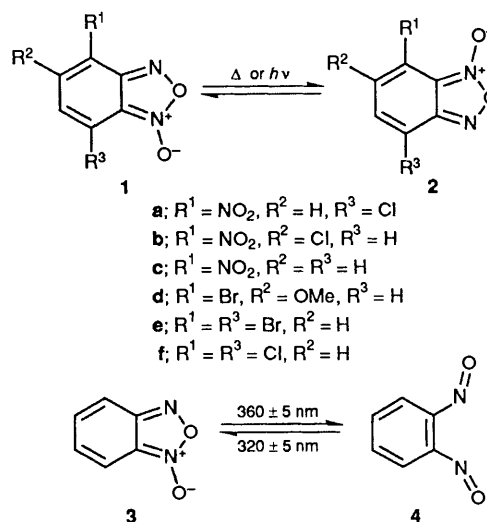
Finally, further support for the identity of 4 came from the matrix photolysis of 2-nitrophenyl azide 7.[4] Photolysis of 7 in an Ar matrix (λ 330 ± 5 nm) gave a mixture of 3 and 4, presumably via 2-nitrophenylnitrene. Irradiation of the resulting matrix with 320 or 356 nm light increased the proportions of 3 or 4, respectively, in exactly the same way as observed in the other experiments. Thus, the thermal[4] and photochemical decompositions of 7 appear to proceed by analogous pathways

Table 1 IR absorptions (v/cm⁻¹) of 3 and 4 in Ar matrices at 14 Kᵃ

3	4	[¹⁴N¹⁵N]-4
1622 s	1516 s	1516 m
1598 s		1501 m
1589 s	1423	1422 m
1545 s	1257	1259
1492 m		1252
1446	1162	1158
1427		1124
1358	1108 m	1103 s
1205	1077	1076
1151 vw	805	802
1126		785
1020 m	772	769
895	622 vw	
837		
760		
746 m		
739		
669		

ᵃ Bands were weak unless shown as s (strong), m (medium), or vw (very weak).

a; R¹ = NO₂, R² = H, R³ = Cl
b; R¹ = NO₂, R² = Cl, R³ = H
c; R¹ = NO₂, R² = R³ = H
d; R¹ = Br, R² = OMe, R³ = H
e; R¹ = R³ = Br, R² = H
f; R¹ = R³ = Cl, R² = H

† Cf. Nitrosobenzene, an authentic sample of which had v(N=O) at 1510 cm⁻¹ (Nujol).
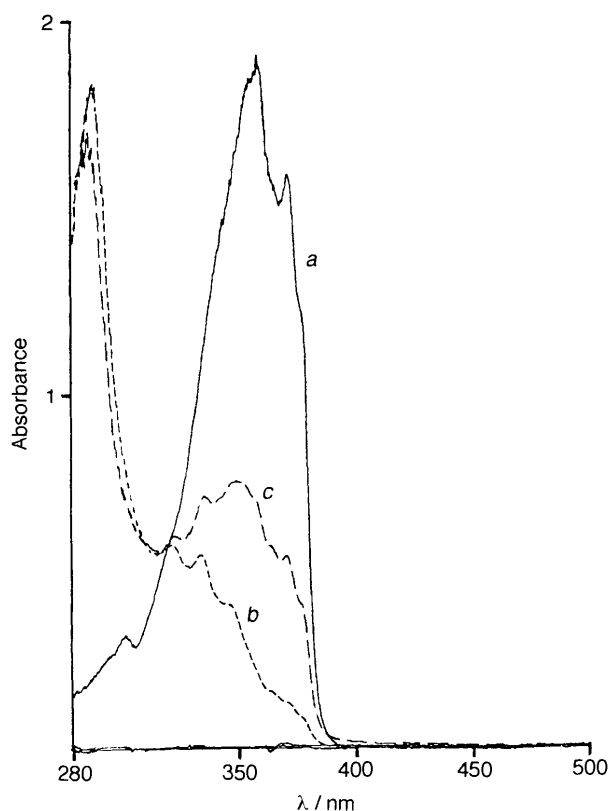
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Fig. 1 UV–VIS absorption spectra in the region 280–500 nm of Ar-matrix isolated benzofurazan 1-oxide **3**; (*a*) immediately after deposition at 14 K, (*b*) after 1 h photolysis with λ 356 ± 5 nm, and (*c*) after a further 1.5 h irradiation with λ 320 ± 5 nm

to the same product **3**. 2-Nitrophenyl azide specifically labelled with ^{15}N at the azide nitrogen attached to the benzene ring was prepared from commercially available ^{15}N-labelled potassium phthalimide (Aldrich, 98 atom%) and 1-bromo-2-nitrobenzene, by Gabriel synthesis to give 2-nitroaniline with the ^{15}N-label in the amino group, followed by diazotization with HNO_2 and reaction of the diazonium salt with sodium azide.[7] Photolysis of the resulting specifically labelled **7** in an Ar matrix led to the formation of a mixture of [$^{14}N^{15}N$]-**3** and [$^{14}N^{15}N$]-**4**, each containing just a single ^{15}N-atom. By photochemical interconversions as described above, it was possible to discriminate between the IR bands of labelled **3** and **4**, and those which could be positively assigned to [$^{14}N^{15}N$]-**4** are listed in Table 1. A number of changes can be
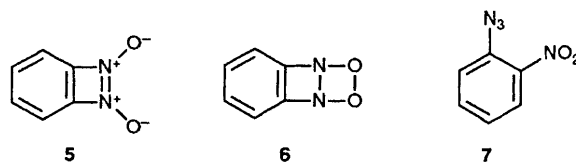
noted in the IR spectrum of the labelled compound, but of paramount significance is that singly labelled **4** has two v(N=O) bands, one unshifted at $1516\ cm^{-1}$, the other at $1501\ cm^{-1}$, with an isotope shift of $-15\ cm^{-1}$. It might have been expected that even unlabelled **4** would show two v(N=O) bands owing to coupling giving rise to an asymmetric and a symmetric stretch. The presence of only one such band suggests that such coupling is very small. This is quite understandable in **4**, where the two nitroso groups can rotate independently giving a fairly floppy molecule, but less so in the much more rigid isomers **5** and **6**. This independence of the two nitroso groups is fully confirmed by the ^{15}N-labelling result. With singly labelled **4**, two distinct v(N=O] bands become visible, but one of these is unshifted within the accuracy of our measurements (a shift of $<1\ cm^{-1}$). Evidence of coupling between the two vibrations, *i.e.* a perceptible isotope shift in both bands, would be expected for the rigid isomers **5** and **6**. All the spectroscopic evidence, therefore, supports the identification of **4** as the matrix photoproduct of **3**.

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5 (*a*) For a general description of the matrix isolation technique and its applications in organic chemistry, see I. R. Dunkin, *Chem. Soc. Rev.*, 1980, **9**, 1; and in *Chemistry and Physics of Matrix Isolated Species*, ed. L. Andrews and M. Moskovits, North-Holland, Amsterdam, 1989, ch. 8, p. 203; (*b*) The matrix isolation equipment was similar to that described in detail previously: I. R. Dunkin and J. G. MacDonald, *J. Chem. Soc., Perkin Trans. 2*, 1984, 2079. Research grade Ar of better than 99.9997% purity was obtained from BOC Ltd. IR spectra were recorded on a Perkin-Elmer 684 spectrometer interfaced with a Perkin-Elmer 3600 Data Station; UV–visible spectra were recorded on a Shimadzu UV250 spectrometer. Photolysis was carried out with an Oriel 200 W high-pressure Hg arc with its beam collimated through an Applied Photophysics high radiance f/3.4 monochromator.
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