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Aromatic Nitro-group Displacement Reactions. Part 6.[1] Structure of the Compound Formed by the Action of Morpholine on 2,2′,4,4′-Tetranitrobenzophenone†

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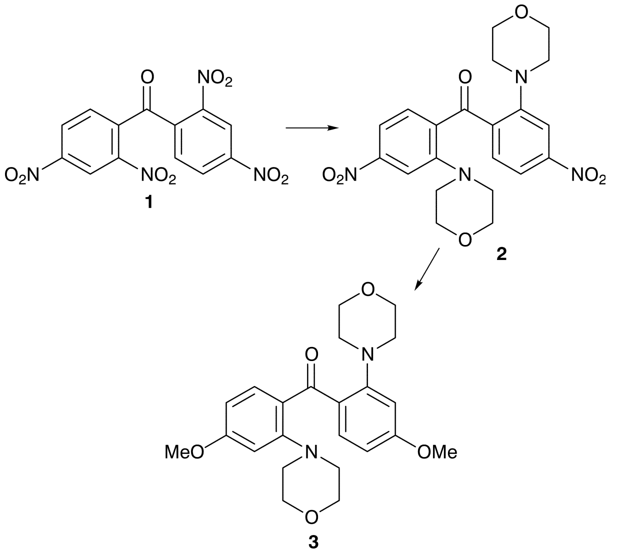
Morpholine has been shown to displace the two *ortho-nitro* groups in 2,2′,4,4′-tetranitrobenzophenone.

The reaction of 2,2′,4,4′-tetranitrobenzophenone **1** with a primary aromatic amine leads initially to the displacement of a 2-nitro group.[1,2] Formation of a 10-arylacridine-9-one may then follow by a cyclodehydronitration involving the 2′-nitro group. With a secondary aliphatic amine such as morpholine, **1** reacted with the independent displacement of two nitro-groups.



On the grounds of earlier arguments[2] we assumed the product to have the structure **2** but this assumption had to be proved. Lack of solubility in cold dimethyl sulfoxide ruled out ^{1}H NMR studies on **2** but the remaining two nitro-groups in **2** were readily replaced by methoxy to yield a compound probably, not definitely, with structure **3**. Earlier ^{1}H NMR studies on **3** failed to give an unequivocal conclusion owing to similarity of chemical shifts and lack of shift parameters for morpholine. The problem can now be resolved by NOE difference studies at higher field.

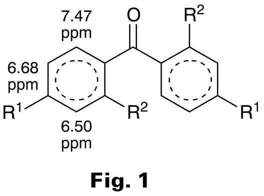


Fig. 1

Table 1

	Observed NOE enhancements at				
Signal irradiated	7.47 ppm	6.68 ppm	6.50 ppm	3.82 ppm	2.60 ppm
7.47 ppm		14%	nil	nil	nil
6.68 ppm	14%		nil	2.5%	nil
6.50 ppm	nil	nil		2.3%	2.3%
3.82 ppm	−1.4%	10%	4.7%		nil

The three aromatic protons of structure **3** (or its possible isomer) form a three-spin system whose couplings allow assignment to the partial structure shown in Fig. 1.

The three aromatic multiplets and the methoxy signal at 3.82 ppm were irradiated in standard NOE difference experiments, giving the enhancements shown in Table 1.

Irradiation of the two CH_2 signals of the morpholine group produced the expected large NOE responses to each other and also the following results shown in Table 2.

Table 2

	Observed NOE enhancements at		
Signal irradiated	7.47 ppm	6.68 ppm	6.50 ppm
2.98 ppm	3.4%	2.5%	nil
2.60 ppm	3.7%	nil	10.4%

Considered together, the observed enhancements are only consistent with a structure which has the methoxy groups at R^1 in the partial structure, as originally proposed. The negative NOE observed on irradiation of the methoxy is a relayed effect (*via* the proton at 6.68 ppm) often seen in such systems.

Experimental

NOE difference spectra were recorded in [$^2H_6$]dimethyl sulfoxide solutions at 400 MHz (Bruker DXR-400).

Reaction of 2,2′,4,4′-*Tetranitrobenzophenone* **1** *with Morpholine.*—The nitro-compound (1.81 g, 0.5 mmol) was refluxed with morpholine (8.7 g, 0.1 mol) for 7 h. Filtration gave 1.48 g (67%) of 2,2′-*dimorpholino*-4,4′-*dinitrobenzophenone* **2**, which formed yellow crystals from DMF–EtOH, mp 285–286 °C (Found: C, 56.7; H, 4.8; N, 12.6. $C_{21}H_{22}N_4O_7$ requires C, 57.0; H, 5.0; N, 12.7%); ν_{max}/cm^{-1} (KBr) 1640 (CO), 1520 and 1351 (NO_2). No other compound was isolated.

4,4′-*Dimethoxy*-2,2′-*dimorpholinobenzophenone* **3**.—To the nitro-compound (3.8 g) in hot dimethyl sulfoxide (100 ml) was added 1 M MeONa–MeOH (25 ml); the solution was left overnight. Addition of water led to the precipitation of the *methoxy compound* **3** (3.5 g) which crystallised from DMF–EtOH, mp 205–206 °C

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

(Found: C, 66.8; H, 6.9; N, 6.7. $C_{23}H_{28}N_2O_5$ requires C, 67.0; H, 6.8; N, 6.8%); ν_{max}/cm^{-1} (KBr) 1635 (CO); *m*/*z* 413 ($M + H^+$).

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