

Crystal Structure of Methyl 1,1,7,9-Tetranitro-2,5-epoxy-1,2,4,5-tetrahydro-3,2-benzoxazepine-4-carboxylate, a Product of Nitration of 2-Methoxy-1-nitronaphthalene

Piotr Balczewski, Roy L. Beddoes and John A. Joule*

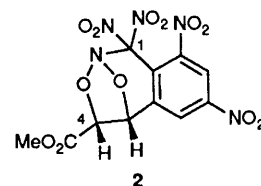
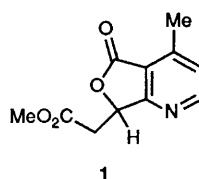
Chemistry Department, University of Manchester, Manchester M13 9PL, UK

The synthesis by the reaction of fuming nitric acid with 2-methoxy-1-nitronaphthalene, and X-ray crystallographic analysis of the tricyclic 1,3,2-dioxazolidine **2** are described.

We have recently described¹ the conversion of 6-methoxy-4-methylquinoline into the aza-phthalide **1**, by treatment with fuming nitric acid. This unexpected transformation prompted an examination of some related bicyclic aromatic compounds under comparable conditions and here we describe the isolation of the tricycle **2** derived from 2-methoxynaphthalene.

Controlled nitration² of 2-methoxynaphthalene produces 2-methoxy-1-nitronaphthalene whilst reaction in fuming nitric acid (-40 to 0 °C)³ gives 2-methoxy-1,6,8-trinitronaphthalene. In order to make a direct comparison with our earlier work¹ we exposed 2-methoxy-1-nitronaphthalene to fuming nitric acid at room temperature for 15 h. Chloroform extraction yielded a crystalline substance (35%) which could be purified by chromatography over silica and which could be recrystallised from ethanol. The same compound was obtained starting from 2-methoxy-1,6,8-trinitronaphthalene.

The new material had UV absorption very similar to that of *m*-dinitrobenzene and an ester carbonyl IR stretching at 1746 cm^{-1} . In addition to ^1H NMR signals for the *m*-dinitroaromatic ring (δ_{H} (CDCl_3) 8.98 and 9.26) and ester methoxy (3.58), there were two doublets (δ_{H} 5.48 and 7.00, J 4.9 Hz) for a pair of vicinal saturated hydrogen atoms. Each of these features was corroborated by ^{13}C signals, for six aromatic, two saturated methine, methoxyl and carbonyl carbons; however no ^{13}C signal could be seen, in either of two solvents, for an



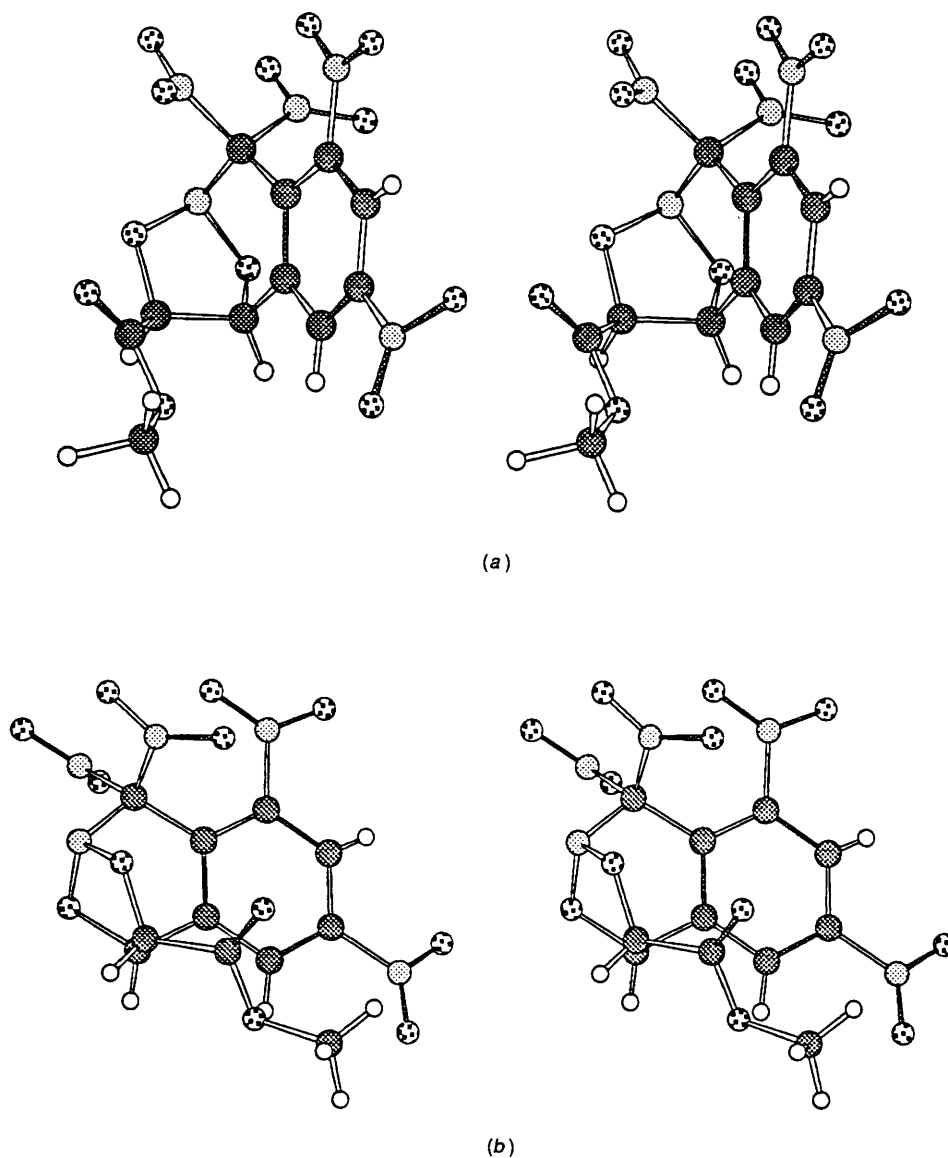


Fig. 1

eleventh carbon to be expected from the formula of the starting 2-methoxy-1-nitronaphthalene and confirmed (a) by a combustion analysis consistent with $C_{11}H_7N_5O_{12}$ for the new material, and (b) by a mass spectral ion at m/z 355, corresponding to $(C_{11}H_7N_5O_{12} - NO_2)$. It was clear that a phthalide, comparable to **1**, had not been obtained⁴ so a suitable crystal was analysed by X-ray crystallography.

The crystal structure,[†] illustrated in the stereoscopic

drawings shown in Fig. 1, shows the 'nitration' product to contain a uniquely situated 1,3,2-dioxazolidine ring and a geminal dinitro group. The aspect shown in Fig. 1 (a) is chosen to illustrate how each aromatic nitro group is essentially in the plane of the benzene ring, and how one of these aromatic nitro groups bisects the geminal pair of nitro groups. The alternative viewpoint shown in Fig. 1(b) shows clearly the *cis*-relationship of the saturated methine hydrogens, with an observed dihedral angle of 35° corresponding to the observed 4.9 Hz coupling constant. Fig. 1(b) also nicely shows the (almost) ideally pyramidal dioxazolidine ring nitrogen: the three bond angles around this nitrogen are 105.8, 106.3, and 106.5° respectively, summing to 318.6° . There are three other crystal structures⁵⁻⁷ in which a ring nitrogen is attached to two oxygen atoms, including one in which the nitrogen is part of a 1-aza-7,8-dioxabicyclo[3.2.1]octane (epoxyoxazepine); in each example the nitrogen is essentially pyramidal with angle sums of 317.4, 310.6, and, for 2,2-difluoro-3-trifluoromethyl-5-methyl-1-aza-7,8-dioxabicyclo[3.2.1]octane,⁷ 318.2° , amazingly close to the value for the more complex structure **2**.

Molecules containing saturated nitrogen complex attached to two oxygen atoms, as in **2**, are rare. 2-Methoxy-3,3-dinitroisoxazolidines were produced by dipolar cycloaddition of alkenes to *O*-methyl ethers of trinitromethane,⁸ a process later extended

[†] Crystal data for **2**: $C_{11}H_7N_5O_{12}$, pale-yellow, m.p. 141–142 °C, with gas evolution, crystal dimensions $0.25 \times 0.30 \times 0.35$ mm, monoclinic, $a = 11.474(2)$, $b = 8.1274(6)$, $c = 16.3678(6)$ Å, $\beta = 103.602(8)^\circ$, $U = 1483.6(3)$ Å³, space group $P2_1/c$ (No. 14), $Z = 4$, $F(000) = 816$. $\omega/2\theta$ scans of $(1.31 + 0.30 \tan \theta)$ were made at a speed of $32.0^\circ \text{ min}^{-1}$ at 298 K; 1914 reflections were collected with $5^\circ < 2\theta < 125^\circ$; of these, 1832 which were unique, and had $F > 6\sigma(F)$, were used in the analysis. The data were collected on a Rigaku AFC5R diffractometer using graphite monochromated Cu-K α radiation. Lorentz, polarisation and linear intensity drift (maximum 2.9%) corrections were applied. The structure was solved by direct methods. The refinement converged with $R = 0.06$, $R_w = 0.078$. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation (1985). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

to ethers of dinitromethane, generating 2-methoxy-3-nitroisoxazolidines.⁹ In compound **2** it is the quaternary benzylic carbon, C-1, carrying two nitro groups and the dioxazolidine ring nitrogen, for which no ¹³C signal was observed; unfortunately no ¹³C data are available for the monocyclic 2-methoxy-3,3-dinitroisoxazolidines,⁸ in which there is a comparably heavily nitrogen-substituted quaternary carbon, C-3.

1,3,2-Dioxazolidines have been synthesised *via* the reaction of ethane-1,2-diol with *N,N*-dimethyl-*N',N'*-dimethoxyurea¹⁰ or by cyclisation of *N*-(2-hydroxyethoxy)-*N*-chloroureas.¹¹ An NMR study of 1,3,2-dioxazolidine itself concluded that the conformation was that of a 'curved envelope';¹² the perspective shown in Fig. 1(b) illustrates how the dioxazolidine ring in **2** does indeed adopt such a conformation, even within the confines of the rigid tricyclic ring system.

The method of preparation, the disposition of nitrogen and oxygens in the dioxazolidine ring, and the *cis*-relationship of the two saturated methine hydrogen atoms all strongly suggest that **2** is formed *via* an intramolecular cycloaddition of one of three nitro groups at (the original) C-1 to a *cis*-double bond between (the original) C-3 and C-4. A species which would have resulted from intramolecular cycloaddition of a nitro group to the 1,3-dipole C:N⁺-N⁻ was suggested as an intermediate in a postulated mechanistic sequence.¹³ Nitrobenzenes were shown to add photochemically to some simple alkenes, such as cyclohexene, norbornene and hex-1-ene, at -70 °C, the cycloadducts being mainly characterised *via* 1,2-diols produced by hydrogenolysis,¹⁴ and thermally to the strained *trans*-double bond of *E,Z*-cycloocta-1,5-diene, key evidence for structure being ¹H NMR signals at δ 4.2 for

the OCH protons.¹⁵ Each of these reports ignored an earlier description¹⁶ of intramolecular cycloaddition of nitro groups to alkene double bonds as in the conversion of dihydropyrans such as **3** into tricyclic 1,3,2-dioxazolidines **4**, and of acyclic nitroalkenes **5** into bicyclic 1,3,2-dioxazolidines such as **6**, for which a crystal structure determination was later described.⁷

Regarding the formation of **2**, the simplest rationalisation rests on the fragmentation (arrows) of an intermediate **7**, which would be generated from 2-methoxy-1,6,8-trinitronaphthalene by addition of nitric acid [NO₂⁺ at C-1 then H₂O (at C-2) then -H⁺] producing **8**, after addition of a further nitronium ion, followed by intramolecular dipolar cycloaddition of a nitro group to the double bond.‡

We thank the SERC for a postdoctoral research assistantship (P. B.) and for funds for the purchase of the Rigaku AFC5R diffractometer. P. B. was on leave from the Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź.

Received, 10th December 1990; Com. 0/05545J

References

- P. Bałczewski, R. L. Beddoes and J. A. Joule, *Acta Crystallogr., Sect. C*, 1991, in the press.
- H. Maehr and J. Smallheer, *J. Am. Chem. Soc.*, 1985, **107**, 2943.
- E. J. van der Kam, *Recl. Trav. Chim. Pays-Bas*, 1926, **45**, 564.
- For other examples of the conversion of bicyclic aromatic compounds into phthalides under nitrating conditions see: W. V. Curran, F. M. Lovell and N. A. Parkinson, *Tetrahedron Lett.*, 1979, 2221; B. S. Joshi, V. R. Hegde, D. Rogers and D. J. Williams, *Tetrahedron Lett.*, 1980, **21**, 1163.
- A. B. Zolotoi, O. A. D'yachenko, I. I. Chervin, V. F. Rudchenko, L. O. Atovmyan and R. G. Kostyanovskii, *Khim. Geterotsikl. Soedin.*, 1985, 1341 (*Chem. Abstr.*, 1986, **105**, 5872).
- R. N. Butler, D. Cunningham, E. G. Marren and P. McArdle, *Tetrahedron Lett.*, 1988, **29**, 3331.
- A. A. Espenbetov, A. I. Yanovskii, Yu. T. Struchkov, L. A. Simonyan and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 607 (*Chem. Abstr.*, 1982, **96**, 217808).
- V. A. Tartakovskii, I. E. Chlenov, S. S. Smagin and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 583 (*Chem. Abstr.*, 1964, **61**, 4335); V. A. Tartakovskii, I. E. Chlenov, G. V. Lagodzinskaya and S. S. Novikov, *Dokl. Akad. Nauk SSSR*, 1965, **161**, 136 (*Chem. Abstr.*, 1965, **62**, 14646).
- V. A. Tartakovskii, I. E. Chlenov, N. S. Morozova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 320 (*Chem. Abstr.*, 1966, **64**, 17567).
- V. F. Rudchenko, V. J. Schevchenko and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1556 (*Chem. Abstr.*, 1988, **109**, 73403).
- V. F. Rudchenko, V. J. Schevchenko and R. G. Kostyanovskii, *Khim. Geterotsikl. Soedin.*, 1989, 393 (*Chem. Abstr.*, 1989, **111**, 232690).
- J. J. Chervin, V. S. Nosova, V. F. Rudchenko, V. J. Schevchenko and R. G. Kostyanovskii, *Khim. Geterotsikl. Soedin.*, 1988, 396 (*Chem. Abstr.*, 1989, **110**, 22960).
- R. Grashey, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 158.
- J. L. Charlton and P. de Mayo, *Can. J. Chem.*, 1968, **46**, 1041; J. L. Charlton, C. C. Liao and P. de Mayo, *J. Am. Chem. Soc.*, 1971, **93**, 2463 and references therein.
- J. Leitich, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 372.
- L. A. Simonyan, N. P. Gambaryan, P. V. Petrovskii and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 370 (*Chem. Abstr.*, 1968, **69**, 52077).
- For the demonstration of such a process in a situation in which 1,3-dipolar cycloaddition of nitro is not possible see: A. Berndt, *Angew. Chem.*, 1968, **80**, 666.

‡ The Russian workers preferred^{7,16} a mechanism involving initial [2 + 2] cycloaddition of N⁺=O to C=C to generate a 4H-1,2-oxazete N-oxide¹⁷ followed by rearrangement to 1,3,2-dioxazolidine.

