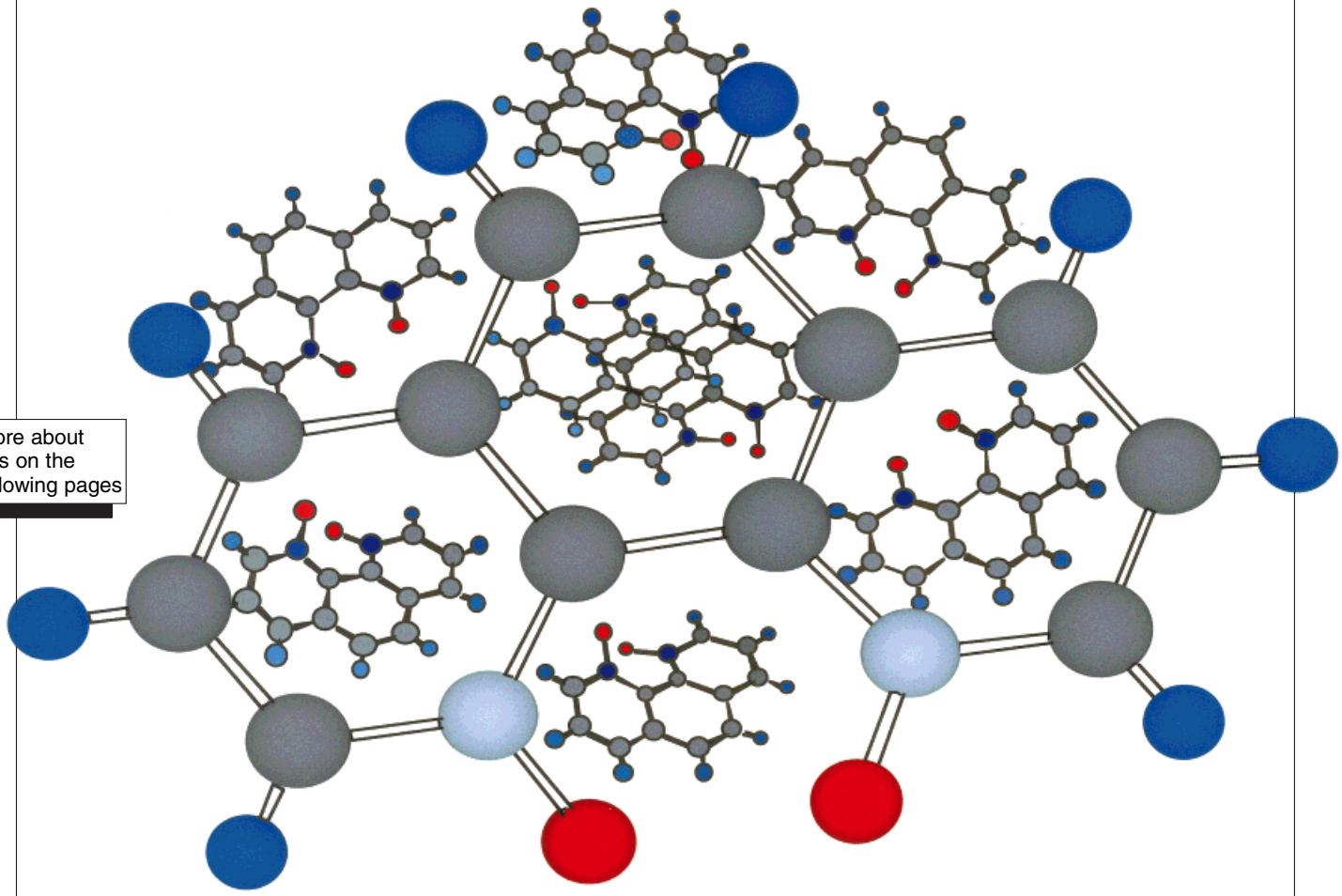
At last, 1,10-phenanthroline-N,N′-dioxide has been prepared with the HOF·CH$_3$CN complex—Probably the best oxygen transfer agent organic chemistry has to offer.



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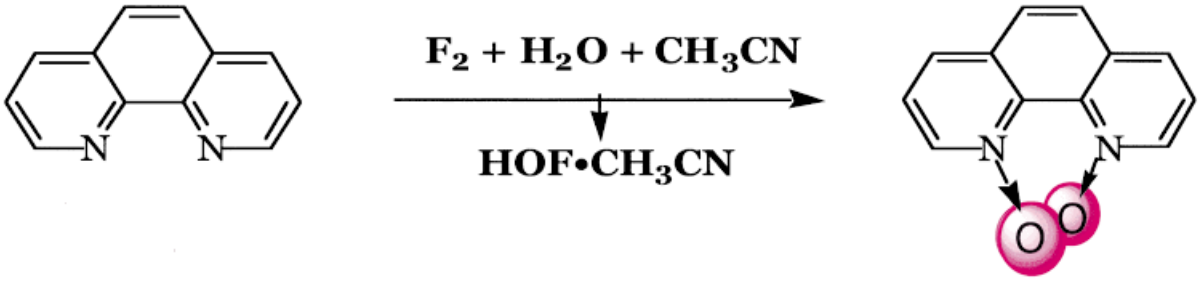

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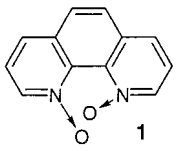
At Last, 1,10-Phenanthroline-*N*,*N*′-dioxide, A New Type of Helicene, has been Synthesized using HOF · CH_3CN**

Shlomo Rozen* and Sharon Dayan

The story of 1,10-phenanthroline-*N*,*N*′-dioxide (**1**) starts more than 50 years ago when Linsker and Evans claimed that **1** could be prepared by simple oxidation of 1,10-phenanthroline (**2**) with hydrogen peroxide.[1] The compound was not characterized and the only support presented was a microanalysis of the corresponding picrate. It did not take long, however, to find out that it was impossible to prepare **1** by this procedure or by any other one. In 1958 Maerker and Case reported that they were unable to prepare the *N*,*N*′-dioxide[2] and a few years later Corey et al. also repeated the synthesis and were only able to get the mono *N*-oxide.[3] Woodward and Wenkert were also interested in obtaining **1**, but they too only got the mono *N*-oxide.[4] Several other attempts were reported[5] which did not change the outcome.



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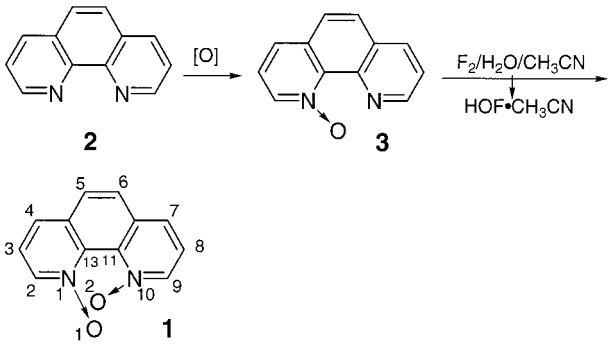
We tried hydrogen peroxide and several peracids, but like all the others, could not get the *N*,*N*′-dioxide. The cumulative failures to prepare **1** convinced Gillard to publish two notes complaining about people erroneously continuing to report the existence of this molecule complexed with a variety of metal ions. He concluded that "all such (reports) are wrong"[6] and the "claims of their existence…should be withdrawn".[7] The reason for the failure of all these attempts is, of course, that the limited space in the bay area of the flat 1,10-phenanthroline molecule cannot accommodate two oxygen atoms. The arsenal of chemical reagents lacked the one that could force the aromatic 1,10-phenanthroline away from planarity, a precondition for a successful synthesis of **1**.

Some years ago[8] we introduced the HOF · CH_3CN complex, which soon became probably the best oxygen-transfer agent in organic chemistry.[9] It is easily prepared by bubbling dilute fluorine through aqueous acetonitrile (see Experimental Section) and is a versatile reagent that operates under very mild conditions. It is able to hydroxylate sp^3 tertiary carbon centers, oxidize alcohols, ethers, ketones, primary aliphatic and aromatic amines, and aromatic rings, as well as epoxidize olefins.[10] It is the only reagent able to oxidize α-amino acids to α-nitrocarboxylic acids[11] and many thiophenes to their *S*,*S*-dioxide derivatives under mild conditions.[12] It also stands alone in its ability to convert very electron-depleted C-C double bonds and sulfides directly into the corresponding epoxides[13] and sulfones.[12] It has been used for the α-hydroxylation of carbonyl compounds and has helped to synthesize some previously impossible indandiones for visualization of fingerprints.[14] Finally HOF · CH_3CN has been used successfully to convert tertiary amines into their *N*-oxides in very good yields.[15] We therefore tried its reaction with 1,10-phenanthroline. We were not disappointed.

Treatment of a solution of 1,10-phenanthroline (**2**) in chloroform with 1.1 equivalents of HOF · CH_3CN at 0 °C for 5 minutes resulted in a good yield of the mono *N*-oxide **3** with traces of a material that was proved later to be the *N*,*N*-dioxide **1** (Scheme 1). Increasing the amount of the HOF · CH_3CN to 2.2 equivalents resulted in an instantaneous yellow



Scheme 1. Synthesis of 1,10-phenanthroline-*N*,*N*′-dioxide with HOF · CH_3CN. [O] = *meta*-chlorobenzoic acid, H_2O_2, or HOF · CH_3CN.

coloration and again the reaction was over in 5 minutes at 0 °C. After recrystallization, the yellow solid was identified as the desired 1,10-phenanthroline-*N*,*N*′-dioxide (**1**). It is a stepwise process as evident from the reaction of the pure mono *N*-oxide **3** with HOF · CH_3CN. In both cases the yield of **1** was higher than 60%. Its picrate melts at 220 °C, which is much higher than that reported by Linsker and Evans (192 °C).[1]

The microanalysis is in agreement with the structure of **1** and the ^{1}H NMR spectrum indicates that the two halves of the molecule are in an identical chemical environment. The signals for H2 and H9 appear at $\delta = 8.58$ (d, $^3J(H,H) = 6.5$ Hz, 2H), a typical value for hydrogens atoms α to an aromatic N→O group. The signals for H4 and H7 are at $\delta = 8.11$ (d, $^3J(H,H) = 8$ Hz, 2H) and the ones for H3 and H8 appear at $\delta = 7.74$ (dd, $^3J_1(H,H) = 6.5$ Hz, $^3J_2(H,H) = 8$ Hz, 2H). The remaining two hydrogen atoms H5 and H6 appear as a singlet at $\delta = 7.83$. The ^{13}C NMR spectrum also points towards a symmetrical structure with the twelve carbon atoms in the structure giving rise to only six signals. The high-resolution mass spectrum is in excellent agreement with the structure of **1**.

The *N*,*N*′-dioxide **1** crystallizes in the space group $P2_1/c$ ($Z = 8$), with two independent molecules in the asymmetric unit. Figure 1 shows that the two oxygen atoms force the whole phenanthroline skeleton away from planarity. Thus while the least squares deviation from plane for 1,10-phenanthroline is only 0.025 Å, the deviation for **1** is 0.52 Å. The torsion angle of O1-N1-C13-C11 was found to be $-14.3(2)°$, while that of O2-N10-C11-C13 was $-14.1(2)°$.[16]

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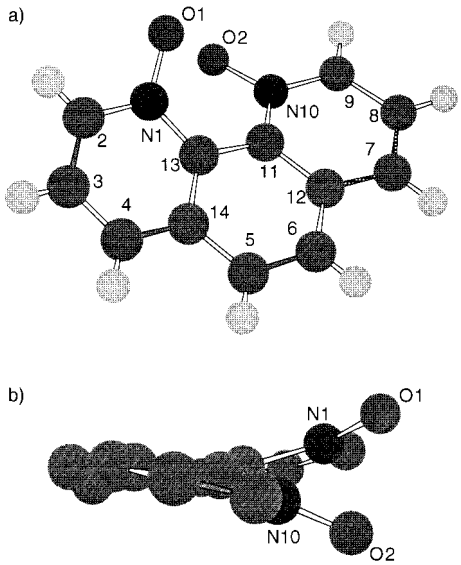

Figure 1. Structure of **1** in the solid state ($R = 0.0555$, $wR2 = 0.1267$). a) View from above; b) side view without hydrogen atoms. Selected bond lengths [Å] and angles [°]:[16] N1-O1 1.297(1), N10-O2 1.315(1), N1-C13 1.391(1), N10-C11 1.383(1), C2-C3 1.388(2), C8-C9 1.388(2), C3-C4 1.381(2), C7-C8 1.382(2), C4-C14 1.404(2), C7-C12 1.403(2), C13-C11 1.440(2), C5-C6 1.354(2), C13-C14 1.413(1), C11-C12 1.418(2), C5-C14 1.441(2), C6-C12 1.437(2), O1-O2 2.5; O1-N1-C2 119.07(9), O1-N1-C13 121.07(9), O2-N10-C9 119.30(9), O2-N10-C11 120.25(9), N1-C13-C14 118.26(9), C11-C13-C14 118.98(10), C5-C14-C13 118.9(10), C6-C5-C14 121.01(10).

The torsion angle of N1-C13-C11-N10 for **2** is less then $-0.5°$, for the monoxide **3** it is $-0.9°$, but for the dioxide **1** the value increases to $-31.7(2)°$. These parameters are responsible for the helical character of the whole molecule (Figure 1b). The individual aromatic rings are also somewhat distorted. While the outer rings are practically identical and show only a modest distortion (the torsion angle N1-C2-C3-C4, for example, is only $2.91(2)°$), the central ring is somewhat less symmetrical and has been forced considerably away from planarity (C13-C11-C12-C6 = $11.98(2)°$ and N1-C13-C14-C5 = $-163.71(1)°$).

The separation of the two oxygen atoms by only 2.5 Å is reflected in the UV spectrum of **1**, which shows a considerable red shift as expected from such a nonbonding interaction: Phenanthroline mono *N*-oxide (**3**) has three main absorptions at 239 nm ($\varepsilon_{max} = 1.9 \times 10^4$), 268 nm ($\varepsilon_{max} = 2.7 \times 10^4$), and 313 nm ($\varepsilon_{max} = 4.6 \times 10^3$), while the *N*,*N*-dioxide **1** absorbs at 232 nm (sh, $\varepsilon_{max} = 1.75 \times 10^4$), 278 nm ($\varepsilon_{max} = 1.3 \times 10^4$), 335 nm ($\varepsilon_{max} = 2.8 \times 10^3$), and 366 nm ($\varepsilon_{max} = 2.1 \times 10^3$).

Experimental Section

^{1}H NMR spectra ($CDCl_3$ or D_2O; TMS) were recorded on a Bruker AC-200 spectrometer; the proton broad-band decoupled ^{13}C NMR spectra ($CDCl_3$; TMS) were recorded at 90.5 MHz. High-resolution mass spectra were measured on a VG micromass 7070H instrument. IR spectra were recorded in $CHCl_3$ or in KBr pellets on a Bruker Vector22 FT-IR spectrophotometer. UV spectra were recorded on a Korton UVIKON 931 spectrophotometer using water as the solvent. A Nonius Kappa CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å) was used for the crystal structure elucidation.

General procedure for working with fluorine: Fluorine is a strong oxidant and a very corrosive material. It should be used only with an appropriate vacuum line such as that described in ref. [15]. For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, which simplifies the process. Working with fluorine is relatively simple if elementary precautions are taken and we have had no bad experiences working with it.

General procedure for producing $HOF \cdot CH_3CN$: Mixtures of 10–15% F_2 with nitrogen were used in this work. They were passed at a rate of about 400 mL min^{-1} through a cold (−10 °C) mixture of CH_3CN (400 mL) and H_2O (40 mL). The development of the oxidizing power was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. Typical concentrations of the oxidizing reagent were around 0.3–0.4 M. These solutions were used as obtained with no further purification or isolation of the reagent.

1: A solution of 1,10-phenanthroline (**2**; 0.5 g) in chloroform (20 mL) at 0 °C was added to 2.2 equivalents of the $HOF \cdot CH_3CN$ solution. After 5 min the mixture was neutralized using a saturated sodium bicarbonate solution, extracted with $CHCl_3$, dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by recrystallization from EtOH/H_2O (1/3) to give 1,10-phenanthroline-*N*,*N*-dioxide (**1**), m.p. 200 °C; IR: $\tilde{\nu}$ = 1221, 1211, 775, 757 cm^{-1}; ^{13}C NMR: δ = 139.5, 133.2, 127.6, 123.1, 121.2, 98.8; HR-MS (EI) *m/z*: 212.0585 [M^+], calcd for $C_{12}H_8N_2O_2$ 212.0586; elemental analysis calcd for $C_{12}H_8N_2O_2$: C 67.92, H 3.80, N 13.20; found: C 67.77, H 4.26, N 12.83. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132810. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[16] The X-ray values reported are the average of the corresponding values of the two independent molecules found in the asymmetric unit. The parameters may vary up to 0.6° and 0.2 Å from each other.

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