The crystal structure of (dimorpholinophosphoryl)carbonitrile oxide

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An X-ray diffraction study of (dimorpholinophosphoryl)carbonitrile oxide (**1**) was carried out. The structure of the nitrile oxide group in compound **1** is more similar to that in fulminic acid (HC≡N→O) than to those in aryl- and hetarylcarbonitrile oxides. The N→O bond in **1** is shorter than those in the latter compounds, and the nitrile oxide fragment is more linear due to an increase in the XCN angle.

Key words: nitrile oxide; (dimorpholinophosphoryl)carbonitrile oxide; structure; chemical stability; X-ray diffraction study.

It is known that the majority of nitrile oxides are chemically unstable and dimerize to give furoxans.[1,2] Only a few sterically hindered arylcarbonitrile oxides, in which two *ortho* substituents are located near the nitrile oxide group, are stable.[1] Furthermore, stable nitrile oxide derivatives of thiophene and benzene, which contain an alkylsulfonyl or sulfonylamide group in only one of the adjacent *ortho* positions, have been reported.[3,4] The stability of these compounds has been rationalized by the interaction of the carbon atom of the nitrile oxide group with the sulfur atom of the sulfonyl group.[4]

We have synthesized (dimorpholinophosphoryl)carbonitrile oxide (**1**), which is highly stable in the crystalline state and in solutions in various organic solvents even on prolonged heating.[5] It does not dimerize under ordinary conditions into either the furoxan or the 1,4-dioxa-2,5-diazine derivative. Attempts to perform its 1,3-dipolar cycloaddition to ketones, aldehydes, imines, nitriles, phosphorylated enamines, and phosphorylated vinyl esters have also failed. Compound **1** does not change in boiling acetonitrile for over 4 h, although analogous (dialkoxyphosphoryl)carbonitrile oxides are known to react with ethylenic and acetylenic dipolarophiles or to dimerize into furoxans.[6] Unlike arylcarbonitrile oxides,[1] compound **1** does not add alcohols, acetic acid, phenol, nitrophenol, or picric acid, but reacts with hydrogen halides,[5] amines, and hydrazines.

To reveal the particular features of the molecular structure of compound **1** and their relation to its chemical properties, we carried out an X-ray diffraction study. The general view of the molecule in a crystal is presented in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2.

The morpholine rings have a chair conformation: the angles of folding about the C(2)···C(6), C(3)···C(5) and C(7)···C(11), C(8)···C(10) lines are 58°, 53° and 40°, 43°, respectively. The deflections of the N(1) and O(4) heteroatoms from the C(2)C(3)C(5)C(6) plane are 0.69(1) and −0.69(1) Å, respectively, while those of the N(2)

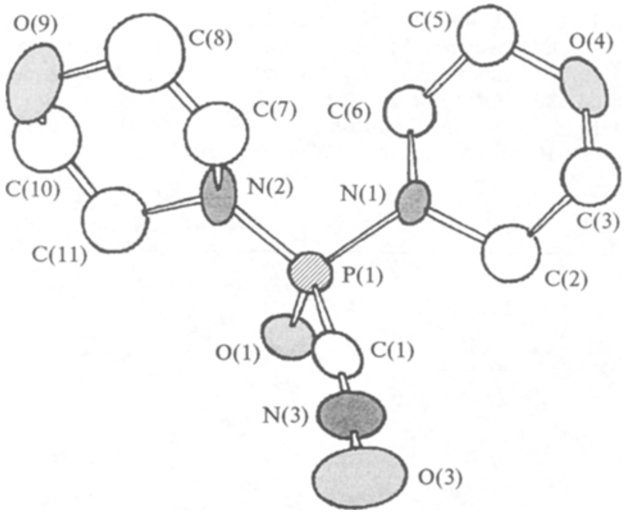

Fig. 1. General view of molecule **1**.

Table 1. Bond lengths in molecule **1**

Bond	*d*/Å	Bond	*d*/Å
P(1)—O(1)	1.465(5)	N(1)—C(2)	1.44(1)
P(1)—N(1)	1.645(7)	N(1)—C(6)	1.51(1)
P(1)—N(2)	1.596(6)	N(2)—C(7)	1.47(1)
P(1)—C(1)	1.83(1)	N(2)—C(11)	1.49(1)
O(3)—N(3)	1.21(1)	N(3)—C(1)	1.13(1)
O(4)—C(3)	1.45(1)	C(2)—C(3)	1.53(1)
O(4)—C(5)	1.45(1)	C(5)—C(6)	1.53(1)
O(9)—C(8)	1.52(2)	C(7)—C(8)	1.32(2)
O(9)—C(10)	1.41(1)	C(10—C(11)	1.38(1)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1245—1247, July, 1994.

Table 2. Bond angles in molecule **1**

Angle	φ/deg	Angle	φ/deg
O(1)P(1)N(1)	118.0(4)	P(1)N(2)C(11)	118.4(7)
O(1)P(1)N(2)	113.4(3)	C(7)N(2)C(11)	112.6(8)
O(1)P(1)C(1)	110.1(4)	O(3)N(3)C(1)	174(1)
N(1)P(1)N(2)	105.8(4)	P(1)C(1)N(3)	175.0(8)
N(1)P(1)C(1)	101.1(4)	N(1)C(2)C(3)	107.6(8)
N(2)P(1)C(1)	107.3(4)	O(4)C(3)C(2)	107.0(9)
C(3)O(4)C(5)	112.8(7)	O(4)C(5)C(6)	107.6(9)
C(8)O(9)C(10)	109.5(9)	N(1)C(6)C(5)	104.3(8)
P(1)N(1)C(2)	118.7(6)	N(2)C(7)C(8)	115(1)
P(1)N(1)C(6)	117.9(6)	O(9)C(8)C(7)	116(1)
C(2)N(1)C(6)	113.4(7)	O(9)C(10)C(11)	117(1)
P(1)N(2)C(7)	120.2(6)	N(2)C(11)C(10)	113(1)

and O(9) atoms from the C(7)C(8)C(10)C(11) plane are −0.53(1) and 0.58(1) Å, respectively.

The configuration of the N atoms in the morpholine rings is noticeably flattened: the degree of pyramidality[7] is $C_p^{N(1)} = 0.25$, $C_p^{N(2)} = 0.22$. However, these values are greater than in the molecules of (*Z*)-2-chloro-1-hydroxy-2-(dimorpholinophosphoryl)ethylene (**2**, $C_p^{N(1)} = 0.10$, $C_p^{N(2)} = 0.16$) and (dimorpholinophosphoryl)dibromomethane[8] (**3**, $C_p^{N(1)} = 0.22$, $C_p^{N(2)} = 0.02$). The orientation of the rings relative to the O=P—C moiety in molecule **1** is different and coincides with that found in molecules **2** and **3**: the torsion angles O=P—N— (the unshared electron pair of the N atom) in compounds **1—3** are −176.3°, 179.4°, and 177.1° for the N(1) atom and −86.2°, 67.6°, and 99.8° for the N(2) atom. The deflections of the bond angles at the P atom in molecules **1**, **2**, and **3** from the ideal tetrahedral angles are comparable. Taking these data into account, it is difficult to explain why there is a marked difference between the P—N(1) and P—N(2) bond lengths [1.645(7) Å and 1.596(6) Å, respectively] in molecule **1**, while these bonds are almost identical in molecules **2** and **3**.

The nitrile oxide moiety in compound **1** is almost linear: the P(1)C(1)N(3) angle is 175.0(8)° and the C(1)N(3)O(3) angle is 174(1)°. According to experimental results and theoretical calculations, fulminic acid also has a linear structure.[9,10] The nitrile oxide moiety in other nitrile oxides studied by the X-ray diffraction method displays marked deviations from linearity due to a decrease in the R—C—N bond angle. For example, this angle is 173.8° in 4-methoxy-2,6-dimethylbenzonitrile oxide (**4**),[11] 171.7° in 4-bromo-2,6-dimethylbenzonitrile oxide (**5**),[12] and 171.8° and 172.3° in 2-(*N,N*-dimethylsulfonylamido)benzo- (**6**) and 5-methyl-2-methylsulfonyl-3-thiophenecarbonitrile oxides (**7**),[4] respectively. This deviation of the nitrile oxide moiety from linearity (the R—C—N angle is less than 175°) in the crystalline state has been attributed either to molecular packing in the crystal[12] or to the contribution of the allene-type mesomeric structure $—C^{-}=N^{+}=O$ to the ground state of the molecule.[13]

Molecule **1** contains a rather short C(1)···C(2) contact equal to 3.045(15) Å. However, the fact that the hydrogen atoms at C(2) were not revealed in the experiment, but were located at positions calculated based on stereochemical considerations did not allow us to reliably consider this contact as an intramolecular hydrogen bond of C—H···C type.

The rather short N(3)→O(3) bond [1.21(1) Å] in molecule **1** is also noteworthy. This bond length is similar to that found in fulminic acid[9] (1.207 Å) and is much shorter[4,11,12] than those in aryl- and thiophenecarbonitrile oxides **4—7**.

The molecular packing in the crystal has no particular features: the intermolecular distances are longer than the sums of the corresponding van der Waals radii. The length of the shortest intermolecular contact O(4)···C(6′) is 3.241 Å.

Thus, the increased chemical stability of compound **1** can be explained by the steric shielding of the nitrile oxide moiety by the bulky morpholine substituents at the phosphoryl group rather than by the presence of a strong electron-withdrawing group at the carbon atom of the nitrile oxide moiety.

Experimental

The crystals of compound **1** ($C_9H_{16}N_3O_4P$, m.p. 104—105 °C) grown from acetonitrile are orthorhombic. At 20 °C, a = 8.758(4), b = 9.353(3), c = 15.433(8) Å, Z = 4, d_{calc} = 1.373 g cm^{-3}, space group $P2_12_12_1$. The cell parameters and the intensities of 550 independent reflections with $F^2 \geq 3\sigma(F^2)$ were measured on an automated four-circle Enraf-Nonius CAD-4 diffractometer having χ-geometry (Mo-Kα, graphite monochromator, θ/2θ-scanning, θ ≤ 25°). The structure was solved by the direct method using the MULTAN program and refined by the least-squares method in the anisotropic approximation. The hydrogen atoms were partly

Table 3. Coordinates of the non-hydrogen atoms (×10^4) in structure **1**

Atom	*x*	*y*	*z*
P(1)	1804(4)	265(4)	6690(3)
O(1)	1610(10)	−590(10)	7478(6)
O(3)	−2500(10)	1100(20)	5658(8)
O(4)	3930(20	4490(10)	6987(8)
O(9)	3850(20)	−2180(10)	4548(7)
N(1)	2590(10)	1860(10)	6780(10)
N(2)	2740(20)	−540(10)	5949(7)
N(3)	−1260(20)	930(20)	5988(8)
C(1)	−60(20)	730(20)	6240(10)
C(2)	1760(30)	2960(20)	7230(10)
C(3)	2280(20)	4400(20)	6860(10)
C(5)	4760(20)	3380(20)	6530(10)
C(6)	4290(20)	1930(20)	6920(10)
C(7)	2750(20)	30(20)	5060(10)
C(8)	3780(30)	−560(30)	4540(20)
C(10)	3910(30)	−2680(30)	5410(10)
C(11)	2840(30)	−2120(20)	5980(10)

revealed from a difference series and partly located at the positions calculated from stereochemical considerations and then taken into account in the final full-matrix refinement. The final divergence factors were R = 0.089 and R_w = 0.110. The coordinates of the non-hydrogen atoms are listed in Table 3. The thermal parameters and the coordinates of the hydrogen atoms are available from the authors.

This work has been financially supported by the Russian Foundation for Basic Research, project No. 93-03-5069.

References

1. Ch. Grundmann and P. Grunanger, *The Nitrile Oxides*, Springer-Verlag, Berlin, 1971, 242.
2. L. I. Khmel'nitskii, S. S. Novikov, and T. I. Godovikova, *Khimiya furoksanov. Reaktsii i primenenie* [*The Chemistry of Furoxans. Reactions and Use*], Nauka, Moscow, 1983, 311 (in Russian).
3. O. O. Mamaeva, F. M. Stoyanovich, and M. M. Krayushkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2081 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1914 (Engl. Transl.)].
4. M. M. Krayushkin, L. G. Vorontsova, M. G. Kurella, and M. A. Kalik, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 725 [*Russ. Chem. Bull.*, 1993, **42**, 689 (Engl. Transl.)].
5. B. I. Buzykin and M. P. Sokolov, *Zh. Obshch. Khim.*, 1992, **62**, 2266 [*J. Gen. Chem. USSR*, 1992, **62** (Engl. Transl.)].
6. R. Zhang and J. Chen, *Synthesis*, 1990, 817.
7. I. A. Litvinov, Yu. T. Struchkov, N. N. Bystrykh, Yu. P. Kitaev, and B. I. Buzykin, *Khim. Geterotsikl. Soedin.*, 1982, 977 [*Chem. Heterocycl. Compd.*, 1982 (Engl. Transl.)].
8. L. F. Chertanova, B. I. Buzykin, and A. A. Gazikasheva, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2730 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1982, **41**, 2162 (Engl. Transl.)].
9. M. Winnerwisser and H. K. Bodensch, *Z. Naturforsch.*, 1967, **22a**, 1724.
10. B. P. Winnerwisser, M. Winnerwisser, and F. Winther, *J. Mol. Spectr.*, 1974, **51**, 65.
11. M. Shiro, M. Yamakawa, T. Kubota, and H. Koyama, *J. Chem. Soc., Chem. Commun.*, 1968, 1409.
12. M. Shiro, M. Yamakawa, and T. Kubota, *Acta Crystallogr.*, 1979, **B35**, 712.
13. *1,3-Dipolar Cycloaddition Chemistry*, Ed. A. Padwa, Wiley-Interscience, New York, 1984, **1**, 302.

Received December 14, 1993