Crystal and molecular structure of 2,5-bis(fluorodinitromethyl)-1,3,4-oxadiazole

*A. S. Batsanov,[a] Yu. T. Struchkov,[a] A. A. Gakh,[b] and A. A. Fainzil'berg[b]**

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

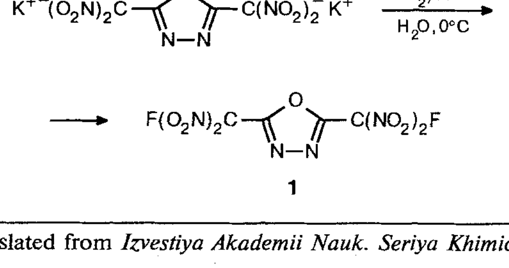
An X-ray structural study of 2,5-bis(fluorodinitromethyl)-1,3,4-oxadiazole (**1**), one of the representatives of azoles with strong electron-withdrawing substituents, has been carried out. It has been found that in the orthorhombic modification of **1** the conformations of the fluorodinitromethyl groups are different. Intermolecular contacts in the crystal are realized through the heterocycles arranged at large angles to each other. The presence of strong electron-withdrawing substituents results in shortening of the C—O bonds and in a certain increase in the OCN angle in the 1,3,4-oxadiazole ring.

Key words: 1,3,4-oxadiazoles, fluorodinitromethyl derivatives, synthesis, X-ray structural method, polymorphism, packing density.

Azoles containing strong electron-withdrawing substituents are of interest due to the possibility that these substituents may considerably affect the structural parameters of the azole ring. Comparison of these «loaded» azoles with normal compounds of this series may be useful for analyzing their chemical properties. In this work we have studied the structure of one of the azoles having strong electron-withdrawing groups: 2,5-bis(fluorodinitromethyl)-1,3,4-oxadiazole (**1**). This compound is of particular interest, since its 1,3,4-oxadiazole ring contains two substituents that possess one of the strongest $-I$ effects ($\rho = 2.53$).[1] Preparation of an analog of **1**, 3,4-bis(fluorodinitromethyl)furoxan,[2] has been reported in the literature. However, the latter compound is a liquid, and it is difficult to carry out an X-ray structural study on it.

Experimental

Compound **1** was prepared in 73 % yield by fluorination of the dipotassium salt of bis(dinitromethyl)-1,3,4-oxadiazole in water. Compound **1** is a colorless crystalline solid, m.p. 49 °C, readily soluble in most organic solvents.



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Crystals suitable for X-ray structural investigation were prepared by careful evaporation of saturated solutions of compound **1** in hexane or in hexane—CCl_4 mixtures. Compound **1** crystallizes (depending on the conditions) in two modifications, one of which is metastable and disintegrates to form a powder when stored in air for several weeks. The structural study was carried out for the stable rhombic form (prepared by crystallization from hexane).

X-Ray diffraction analysis was carried out at −120 °C* on a Syntex $P2_1$ four-circle automatic diffractometer (λMo-$K\alpha$, graphite monochromator), and the calculations were performed on an Eclipse S/200 computer using INEXTL programs.[3] At −120 °C crystals of the orthorhombic modification have the following parameters: a = 6.014(1), b = 9.308(2), c = 18.417(3) Å; V = 1030.9(3) Å^3; space group $Pca2_1$, Z = 4, d_{calc} = 2.024 g cm^{-3}. The intensities of 1004 independent reflections with $I \geq 2\sigma(I)$ were measured $\theta/2\theta$ ($2\theta \leq 55°$). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic-isotropic approximation (hydrogen atoms) to R = 0.028 (R_w = 0.048) with the weight scheme $w = 1/[\sigma^2(F_{meas})+(0.02F_{meas})^2]$. Atomic coordinates are given

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* Determination of the unit cell parameters of the rhombic modification of **1** at room temperature proved to be difficult due to the low melting point (49 °C) and not very accurate: a = 5.98(3), b = 9.83(6), c = 18.48(6) Å; V = 1088(6) Å^3. These values account for d_{calc} = 1.92(1) g cm^{-3} at 25 °C. A 5 % increase in the unit cell volume over the temperature range 153—298 K is normal for molecular crystals (see Ref. 4).

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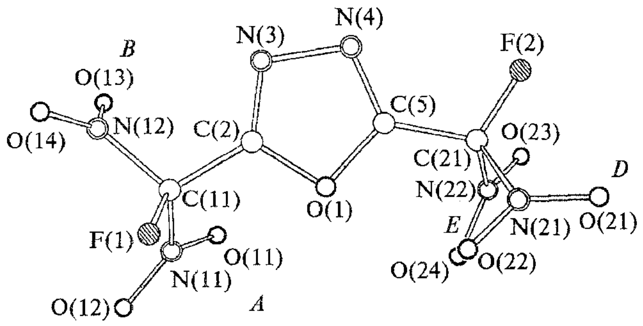

Fig. 1. Projection of molecule **1** onto the plane of the heterocycle.

in Table 1, the structure of molecule in crystal is shown in Fig. 1.

Results and Discussion

The oxadiazole ring in molecule **1** (Fig. 1) is planar. The C(11) and C(21) exocyclic atoms deviate slightly from the plane (by +0.05 and −0.04 Å). Average bond lengths in the ring (C—O 1.352(4), C=N 1.286(4), and N—N 1.406(5) Å) are close to those found in the previously investigated similar structures: 2-(5-phenyl-1,3,4-oxadiazolyl-2)benzoic acid[5] and 2-(4-methoxybenzyl)-5-phenyl-1,3,4-oxadiazole[6] (average C—O are 1.365(3); C=N are 1.286(4), and N—N are 1.410(5) Å).

Table 1. Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters $B_{\text{equiv}} = 1/3\ \Sigma B_{y} a_i^* a_j^* (a_i a_j)$

Atom	x	y	z	B_{equiv}
O(1)	6016(2)	2417(2)	427(4)	1.67(5)
C(2)	5571(2)	3136(3)	−965(5)	1.52(7)
N(3)	5844(2)	4286(3)	−1784(4)	1.51(6)
N(4)	6550(2)	4372(3)	−906(4)	1.46(5)
C(5)	6612(2)	3267(3)	371(5)	1.39(6)
F(1)	4416	2641(2)	490(3)	2.38(5)
O(11)	5384(2)	597(3)	−3016(5)	2.79(6)
O(12)	4285(2)	325(3)	−1764(4)	2.84(6)
O(13)	4704(2)	3211(4)	−5022(4)	3.26(7)
O(14)	3969(2)	4208(3)	−2656(5)	3.16(7)
N(11)	4838(2)	996(3)	−2100(5)	1.89(6)
N(12)	4455(2)	3418(3)	−3195(4)	1.90(6)
C(11)	4821(3)	2572(3)	−1313(5)	1.62(7)
F(2)	7791(2)	3841(2)	1341(4)	2.46(5)
O(21)	7694(2)	2770(3)	5273(5)	3.04(7)
O(22)	6549(2)	2375(3)	4719(4)	2.16(6)
O(23)	8155(2)	1423(4)	−133(6)	3.92(9)
O(24)	7176(2)	393(3)	1183(5)	3.19(7)
N(21)	7159(2)	2663(3)	4133(5)	1.70(6)
N(22)	7574(2)	1410(3)	801(5)	2.12(7)
C(21)	7285(2)	2879(3)	1623(5)	1.58(7)

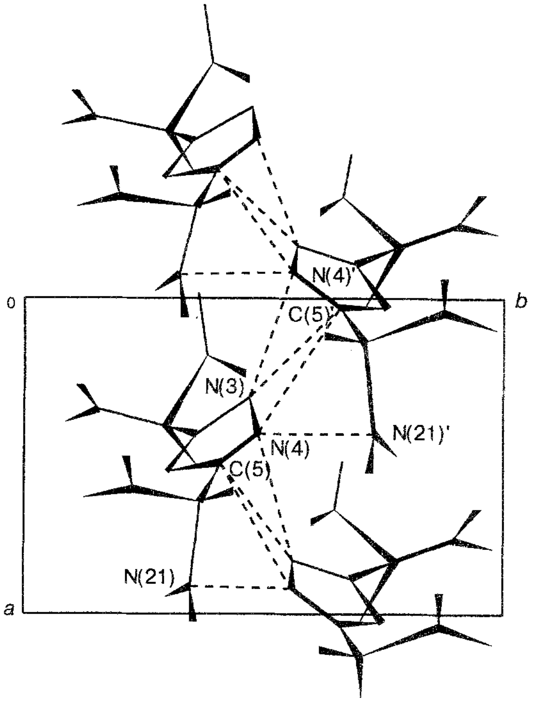

Fig. 2. The packing of molecule **1** in crystal, projection onto the (001) plane.

Thus, the effect of two powerful electron-withdrawing fluorodinitromethyl groups is small and is only exhibited as slight shortening of the C—O bonds and some increase in the OCN endocyclic angles (114.3(3)° in **1** compared with 112.4(3)°, on average, in similar compounds[5,6]). It is of interest that the formally equivalent fluorodinitromethyl groups in molecule **1** have different orientations in crystal; the O(1)C(2)C(11)F(1) and O(1)C(5)C(21)F(2) torsion angles are 66.2(4)° and 180.0(5)°, respectively. All four nitro groups are noticeably tilted with respect to the plane ring (66.2° for group A, see Fig. 1; 74.5° for group B, 42.2° for group D, and 63.9° for group E). Thus, molecule **1** loses its own symmetry in crystal (2 or *mm*2), which is apparently due to intermolecular interactions.

The peculiarity of the packing of compound **1** in a crystal (Fig. 2) is identical to that of some previously studied azoles with two electron-withdrawing groups. For example in 3,5-dinitroisooxazole[7] the heterocycles of neighboring molecules (in this case, those related by the $a(x, 1/2, z)$ symmetry plane) are arranged at a great angle to one another (63°). The shortest contacts between these molecules (N(3)· · ·N(4)′ 3.065(5), N(3)· · ·C(5)′ 3.180(6), N(4)· · ·C(5)′ 3.139(6), and N(4)· · ·N(21)′ 2.979(5) Å) are somewhat less than the sum of the van der Waals radii (3.10 Å for N· · ·N and 3.30 Å for N· · ·C[8]), which may indicate *n*-π-interaction between the heterocycles; the other intermolecular contacts are normal.

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