STRUCTURE OF ORGANIC COMPOUNDS

Crystal and Molecular Structure of a *co*-Crystal of 5-Nitrimino-1,4*H*-1,2,4-triazole with Dimethyl Sulfoxide

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Abstract—The structure of the labile co-crystal of 5-nitrimino-1,4*H*-1,2,4-triazole with dimethyl sulfoxide was determined by X-ray diffraction. It was established that the molecule, previously known as 3(5)-nitramino-1,2,4-triazole, has a nitrimine structure. The geometric parameters of the molecules are similar to those of other nitrimino-1,2,4-triazoles. Intermolecular interactions in the co-crystal are considered. An explanation is provided for the lability of the co-crystal.

INTRODUCTION

The nitrimine structure of a series of compounds, which have previously been considered as nitramino-1,2,4-triazoles [1−5], was unequivocally established by X-ray diffraction. However, the assumption that 5-nitramino-3-nitro-1*H*-1,2,4-triazole [1, 3] has a nitrimine structure was not confirmed. According to the X-ray diffraction data, this compound has a primary nitramine structure [6].

Meanwhile, unsubstituted 3(5)-nitramino-1,2,4-triazole [7] (in actual fact, 5-nitrimino-1,4*H*-1,2,4-triazole) (**I**) was not characterized by X-ray diffraction due to difficulties of the preparation of single crystals suitable for the X-ray diffraction analysis [1, 3]
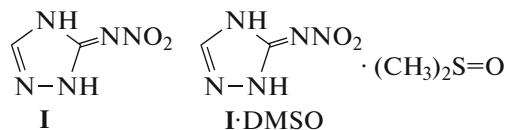
When searching for solvents suitable for growing crystals of compound **I**, we found that the crystallization from dimethyl sulfoxide (DMSO) resulted in the formation of colorless transparent crystals of the solvate **I·DMSO**. According to external signs, these crystals could be suitable for X-ray diffraction. However, the solvate **I·DMSO** proved to be unstable. Thus, the isolation from the solution and washing on a filter with water or an organic solvent led to the disintegration of the crystals to form a finely dispersed powder of compound **I**. The drying of the solvate **I·DMSO** in air directly on a filter, without pre-washing, gave the same result.

Nevertheless, we succeeded in performing the X-ray diffraction analysis of the co-crystal **I·DMSO**. Here we report the crystal and molecular structure of this compound.

EXPERIMENTAL

Compound **I** was synthesized by the nitration of 5-amino-1,2,4-triazole [7]. Transparent crystals of the solvate **I·DMSO** suitable for X-ray diffraction were obtained by the recrystallization of compound **I** from DMSO and were used for the X-ray crystallographic analysis immediately after the filtration from the solution, without washing on a filter or drying.

The X-ray diffraction data were collected at room temperature according to the standard procedure on a KUMA Diffraction KM-4 automatic diffractometer (CuK_α radiation, graphite monochromator, $\theta−2\theta$-scan technique). The crystallographic data and the X-ray diffraction data collection statistics are given in Table 1. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for non-hydrogen atoms (isotropic displacement parameters for hydrogen atoms) using the SHELX-97 program package [8]. Hydrogen atoms were located in difference electron density maps and were refined using a riding model. Selected bond lengths and bond angles are given in Table 2. The molecular geometry and the atomic numbering scheme for the co-crystal **I·DMSO** are presented in Fig. 1. The geometric parameters of intra- and intermolecular hydrogen bonds are given in Table 3.

Table 1. Crystallographic data and the X-ray diffraction data collection and structure refinement statistics for the co-crystals **I**·DMSO

Molecular formula	$C_2H_3N_5O_2 \cdot C_2H_6SO$
Molecular weight	207.21
Temperature, K	298(1)
Sp. gr.; Z	$P2_1/c$; 8
a, b, c, Å	10.078(2), 9.270(2), 19.660(4)
β, deg	104.78(3)
V, Å^3	1775.8(7)
d_x, g/cm^3	1.550
μ, mm^{-1}	3.204
$2\theta_{max}$, deg	130
Number of measured reflections	3018
Number of unique reflections	3017
Number of reflections with $F > 4\sigma_F$	1573
Index ranges h, k, l	$-11 \le h \le 11$; $0 \le k \le 10$; $0 \le l \le 23$
Weighting scheme in the refinement based on F^2	$W = [\sigma^2 + (0.083P)^2 + 0.423P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$
Number of refined parameters	256
$R1$ [$F_o > 4\sigma(F_o)$]	0.0413
$wR2$	0.1163
Extinction parameter	0.0021(3)
S	0.997
$(\Delta\rho)_{max}$, e/Å^3	0.38
$(\Delta\rho)_{min}$, e/Å^3	-0.32
$(\Delta/\sigma)_{max}$	0.0

The CIF file containing the complete information on the structure was deposited with the Cambridge Crystallographic Data Centre (CCDC 1008925) and is available, free of charge, at www.ccdc.cam.ac.uk/data_request/cif.

In view of the lability of the solvate **I**·DMSO, only unique reflections were measured, since the measurement of equivalent reflections leads to an increase in the data collection time and a significant impairment of the quality of the experimental data. For this reason, we ignored the absorption (it was also impossible to apply an analytical correction for absorption because of the non-spherical shape of the crystal).

RESULTS AND DISCUSSION

It should be noted that the established location of protons on nitrogen atoms of the triazole ring (Fig. 1) is an unambiguous evidence for the nitrimine structure of compound **I**.

The co-crystal contains two types of molecules of compound **I** (designated as molecules *A* and *B*) and DMSO. Both types have similar geometric parameters (Table 1), which are equal within the threefold experimental error to the corresponding parameters of the other known nitrimino-1,2,4-triazoles determined by X-ray diffraction, namely, 3-methyl-5-nitrimino-1,4*H*-1,2,4-triazole [1, 3] and bis-3,3'-(5,5'-dinitrimino-1,4*H*-1,2,4-triazolyl)methane [4]. Evidently, slight differences in the observed geometric parameters are not only due to the error in their determination but also to different intermolecular interactions in the compounds under consideration. The latter exert a significant effect on the geometric parameters of nitrimine molecules [9, 10].

Like in other nitrimino-1,2,4-triazoles, the triazole ring and the conjugated nitrimino group in compound **I** have a planar geometry. The root-mean-square deviations of the atoms from the plane of the iminotriazole moiety are 0.002 Å (molecule *A*) and 0.004 Å (molecule *B*). The nitro group is slightly rotated (2.1(3)° for molecule *A* and 1.3(3)° for molecule *B*) about the iminotriazole moiety, and the deviations of the nitro oxygen atoms from its plane vary from 0.023 Å (molecule *B*) to 0.048 Å (molecule *A*).
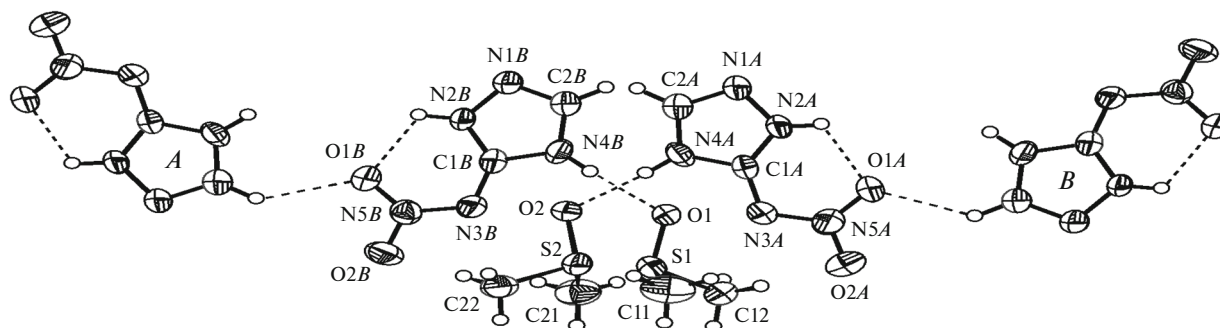

Fig. 1. Geometry of the molecules in the co-crystal **I**·DMSO. Intra- and intermolecular hydrogen bonds are indicated by dashed lines.

Table 2. Selected bond lengths d and bond angles ω

Bond	d, Å	Bond	d, Å
S1−O1	1.507(2)	S2−O2	1.524(2)
S1−C11	1.769(3)	S2−C21	1.768(3)
S1−C12	1.771(3)	S2−C22	1.761(3)
C1A−N4A	1.343(3)	C1B−N4B	1.341(3)
C1A−N2A	1.320(3)	C1B−N2B	1.328(3)
C1A−N3A	1.347(3)	C1B−N3B	1.352(3)
C2A−N4A	1.349(3)	C2B−N4B	1.350(3)
C2A−N1A	1.291(3)	C2B−N1B	1.290(3)
N1A−N2A	1.376(3)	N1B−N2B	1.364(3)
N3A−N5A	1.335(3)	N3B−N5B	1.320(3)
N5A−O1A	1.246(3)	N5B−O1B	1.241(3)
N5A−O2A	1.234(3)	N5B−O2B	1.240(3)
Angle	ω, deg	Angle	ω, deg
O1−S1−C11	105.86(13)	O2−S2−C21	106.45(12)
O1−S1−C12	106.10(10)	O2−S2−C22	106.33(11)
C11−S1−C12	98.81(16)	C21−S2−C22	96.93(14)
N2A−C1A−N4A	105.3(2)	N2B−C1B−N4B	105.1(2)
N4A−C1A−N3A	119.6(2)	N4B−C1B−N3B	120.3(2)
N2A−C1A−N3A	135.1(2)	N2B−C1B−N3B	134.6(2)
N4A−C2A−N1A	112.3(2)	N4B−C2B−N1B	111.9(2)
C1A−N4A−C2A	107.2(2)	C1B−N4B−C2B	107.3(2)
C1A−N2A−N1A	112.1(2)	C1B−N2B−N1B	111.9(2)
C2A−N1A−N2A	103.2(2)	C2B−N1B−N2B	103.8(2)
C1A−N3A−N5A	114.8(2)	C1B−N3B−N5B	115.2(2)
O1A−N5A−O2A	121.5(2)	O1B−N5B−O2B	120.5(2)
N3A−N5A−O1A	121.5(2)	N3B−N5B−O1B	122.5(2)
N3A−N5A−O2A	116.9(2)	N3B−N5B−O2B	117.0(2)

Table 3. Geometric parameters of D−H···A hydrogen bonds in the crystal structure of complex **I**·DMSO

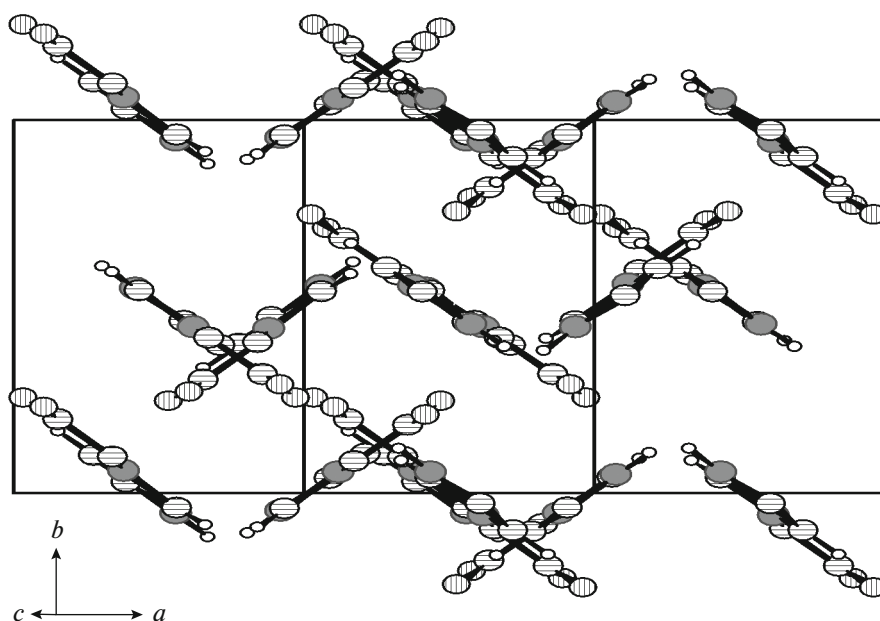| D−H	$d(D$−H), Å	d(H···A), Å	∠DHA, deg	$d(D$···A), Å	A	Symmetry code for atom A
N4A−H4A	0.89(3)	1.89(3)	175(3)	2.775(3)	O2	
N4B−H4B	0.84(3)	1.96(3)	175(3)	2.790(3)	O1	
N2A−H2A	0.83(2)	2.04(2)	117(2)	2.526(3)	O1A	
N2A−H2A	0.83(2)	2.16(2)	153(2)	2.928(2)	O1	$2 − x, 1 − y, 1 − z$
N2B−H2B	0.78(3)	2.10(3)	116(2)	2.540(3)	O1B	
N2B−H2B	0.78(3)	2.19(3)	157(3)	2.920(4)	O2	$1 − x, −y, 1 − z$
C2A−H(C2A)	0.93	2.29	132	2.987(3)	O1B	$1 − x, −y, 1 − z$
C2B−H(C2B)	0.93	2.27	131	2.963(3)	O1A	$2 − x, 1 − y, 1 − z$

Fig. 2. Arrangement of molecules **I** in the unit cell of the crystal of the solvate **I**·DMSO.

As in the above nitrimino-1,2,4-triazoles, as well as in other cyclic and acyclic nitrimines characterized by X-ray diffraction [11], the $C=NNO_2$ bond in molecule **I** is formally double, but it is not actually the case. This bond is even somewhat longer than the other C−N bonds in the conjugated guanidine moiety.
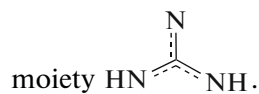
Overall, based on the planar geometry and the experimental bond lengths, the structure of compound **I** can be represented as follows:

I
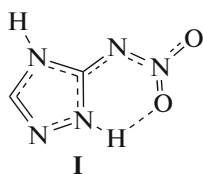
In compound **I** only the N_2-C_3 bond of the triazole ring (here N(1*A*, *B*)−C(2*A*, *B*) according to Fig. 1 and Table 2) corresponds to the criteria of double-bond character. The other C−N, N−N, and N−O bond lengths are intermediate between the values typical of the corresponding single and double bonds. This is indicative of the π-electron density delocalization over the whole molecule of compound **I**.

An intramolecular hydrogen bond, which stabilizes the planar molecular geometry, is another characteristic feature of nitrimines observed in compound **I**. The geometric parameters of these bonds in compound **I** (Table 3) are within the ranges of the corresponding bonds in other nitrimines [12].

The arrangement of molecules **I** in the unit cell of the co-crystal **I**·DMSO is shown in Fig. 2. Molecules **I** lie in the mutually perpendicular layers, both the molecules *A* and *B* and the sulfoxide moieties of DMSO molecules being present in both sets of layers. The intersection line of the layers is perpendicular to the *ab* plane of the crystal structure. The [102] direction coincides with a twofold axis of pseudosymmetry that relates molecules **I** (*A* and *B*) lying in the adjacent parallel layers and DMSO molecules to form pairs. The layers of molecules **I** alternating with the layers of DMSO molecules are parallel to the *ab* plane.

In the co-crystal **I**·DMSO, the molecules of compound **I** are hydrogen-bonded to the DMSO molecules. The strongest hydrogen bond is observed between oxygen atoms of DMSO and the hydrogen atoms attached to the nitrogen atoms at the N_4 position of the triazole ring (here H4*A*, *B* and N4*A*, *B*) (Table 3, Fig. 1). It is known that it is this hydrogen atom, at which the monodeprotonation of molecule **I** occurs, resulting in the formation of salts of compound **I** [3]. Hence, it is not surprising that DMSO, which behaves as a base in the presence of acids, forms such a hydrogen bond with molecule **I**. A weaker hydrogen bond is present between oxygen atoms of DMSO and the hydrogen atoms at the N_1 position of the triazole ring of another molecule **I** (here H2*A*, *B* and N2*A*, *B*) (Table 3). These hydrogen atoms are also involved in the above intramolecular hydrogen bond. Therefore, there is a bifurcated hydrogen bond in the co-crystal **I**·DMSO. Besides, there is apparently an even weaker intermolecular hydrogen bond between the oxygen atoms O1*A*, *B* of the nitro group (which are
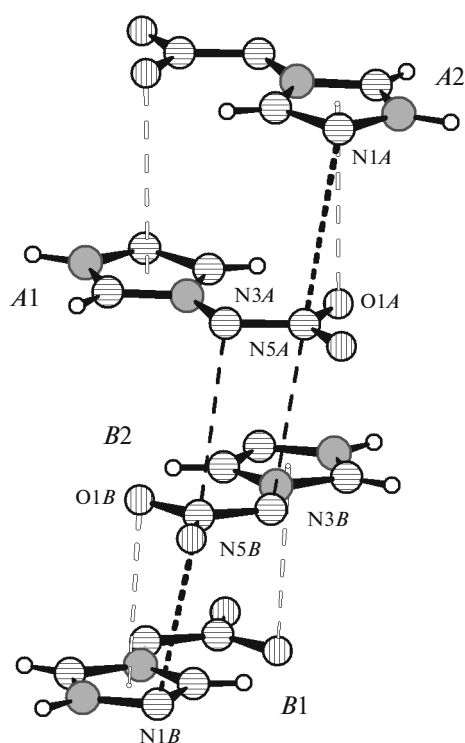
Fig. 3. Supramolecular interaction of the π-conjugated molecular orbital of the 1,2,4-triazole ring with the nitro oxygen atom and the stacking arrangement of molecules **I**.

also involved in the intramolecular hydrogen bond) and the hydrogen atom attached to the carbon atom (Fig. 1, Table 2). These bond lengths (2.27–2.29 Å) are somewhat larger than those satisfying the geometric criteria of hydrogen bonds [13]. However, in the modern energy approach to the evaluation of the existence of hydrogen bonds, there are no strict limits for hydrogen bonding; no rigorous and unambiguous geometric criteria of hydrogen bonds were suggested as well [14]. Therefore, it possible to say that this bond is present in the co-crystal **I**·DMSO.

Intermolecular hydrogen bonds are formed only in the plane within the layers. Interlayer bonds occur through a supramolecular O···triazole ring interaction between molecules $A–A$ and $B–B$ (Fig. 3). The distance between the O1A atom and the centroid of the triazole ring is 3.481(4) Å; between the O1B atom and the centroid of the triazole ring, 3.463(4) Å. The angle between the perpendicular to the plane of the triazole ring and the line between the O1A, O1B atoms and the centroid of the triazole ring is 8.60° and 7.98° for O1A and O1B, respectively.

Besides, there are ...A...A...B...B... stacks of the alternating A and B molecules in the crystal structure of **I** (Fig. 3). The contacts between the molecules A···B (B···A) are as follows: N5A···N3B, 3.306(3) Å; N5B···N3A, 3.339(3) Å. By contrast, the distances

between the molecules of the same type (A···A or B···B) are significantly larger (N5A···N1A, 3.464(3) Å; N5B···N1B, 3.457(3) Å), i.e., the stacks are separated into dimers. This is often observed in the packing arrangements of planar molecules, for example in [15].

The structural features of the co-crystal **I**·DMSO account for the fact that the crystals are easily destroyed upon the addition of solvents or during the storage in air. Dimethyl sulfoxide is a relatively low-volatile, high-boiling-point solvent (T_b = 189°C) due to the formation of strong intermolecular S···O bonds between highly polar DMSO molecules [16]. In the co-crystal **I**·DMSO, these bonds are absent. Therefore, DMSO molecules, which are linked to molecules **I** only by a weaker hydrogen bond, can be rather easily removed from the complex during drying. In the presence of protic solvents, there are competitive solvation interactions with both protophilic DMSO and molecules **I** in the co-crystal **I**·DMSO, which are energetically more favorable than the formation of bonds between molecules **I** and DMSO. In the absence of intermolecular hydrogen bonds between the planar layers of molecules **I** in the co-crystal **I**·DMSO, this leads to the easy destruction of the solvate complex.

In conclusion, despite the lability of the solvate **I**·DMSO and the related experimental difficulties, we succeeded in studying the solvate by X-ray diffraction, which made it possible to unambiguously establish the nitrimine structure of compound **I**.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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