

CRYSTAL STRUCTURE OF S,S'-DIMETHYL-N-NITROIMIDODITHIOCARBONATE

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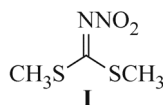
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The molecule of S,S'-dimethyl-N-nitroimidodithiocarbonate has a planar geometry (with the exception of hydrogen atoms of methyl groups), stabilized by the shortened S...O contact. The bond lengths in the >C=N-NO₂ nitrimine moiety, in contrast to nitroguanidine derivatives, make it possible to consider the molecular structure of the compound within the traditional valence formula. The crystal structural feature of the compound is a low energy of its crystal lattice.

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In the S,S'-dimethyl-N-nitroimidodithiocarbonate molecule (**I**), the nitrimine group is bonded to two methylthio groups that relatively easily leave the molecule in nucleophilic substitution reactions.



This allows the preparation of nitroguanidine derivatives with various substituents, which are used for the synthesis of biologically active and energetic substances, from compound **I** by its reaction with amines [1-3].

In the present work, the crystal and molecular structure of compound **I**, which was determined by single crystal X-ray diffraction, is discussed.

Experimental. Compound **I** was synthesized by the method [4]. Transparent crystals suitable for the X-ray crystallographic analysis were obtained by recrystallization from ethanol.

The intensities of 5666 reflections (1774 independent) were measured on an automated Bruker Smart Apex II diffractometer at a temperature of 296(1) K (MoK_α radiation, CCD detector). The model of the structure was solved by direct methods and refined by the full-matrix least squares technique in the anisotropic approximation (isotropic for hydrogen atoms) using the SHELX-97 software package [5]. The hydrogen atoms were located from the difference electron density map, and their sites were further refined under the conditions of a rigid bond with carbon atoms.

The crystals of compound **I**, C₃H₆N₂O₂S₂, are monoclinic, space group *P*2₁/*c*, *a* = 7.394(7) Å, *b* = 13.413(13) Å, *c* = 7.722(8) Å, β = 114.47(1)°, *V* = 697(1) Å³, *Z* = 4, ρ_{calcd} = 1.584 g/cm³, μ_{Mo} = 0.69 mm⁻¹, *M* = 166.22. The resulting values are: *wR*² = 8.35, *S* = 1.04, *R*₁ = 0.066 for all 1774 reflections (2θ_{max} = 57.35°) and *R*₁ = 0.033 for 1079 reflections at |*F*| > 4σ_{*F*}. The interatomic distances and bond angles for all non-hydrogen atoms are listed in Table 1.

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TABLE 1. Bond Lengths d (Å) and Bond Angles ω (deg) in the Structure of Compound **I**


Bond	d	Bond	d	Angle	ω	Angle	ω
N(1)–N(2)	1.395(3)	S(1)–C(2)	1.792(3)	N(1)–N(2)–C(1)	117.3(2)	C(1)–S(2)–C(3)	102.9(1)
N(2)–C(1)	1.312(3)	S(2)–C(3)	1.790(3)	N(2)–C(1)–S(1)	128.5(2)	N(2)–N(1)–O(1)	122.1(2)
C(1)–S(1)	1.734(3)	N(1)–O(1)	1.222(2)	N(2)–C(1)–S(2)	115.9(2)	N(2)–N(1)–O(2)	114.0(2)
C(1)–S(2)	1.729(3)	N(1)–O(2)	1.218(2)	S(1)–C(1)–S(2)	115.6(1)	O(1)–N(1)–O(2)	123.8(2)
				C(1)–S(1)–C(2)	103.3(1)		

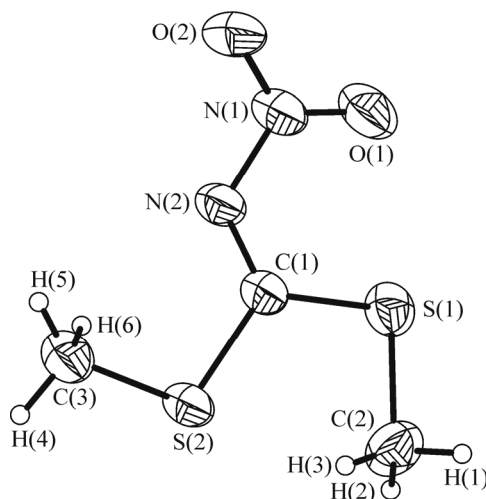
The CIF file containing complete information on the structure studied has been deposited with the Cambridge Crystallographic Data Centre under No. 992497 and can be freely accepted by request via the web-site: www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The general view of the molecular geometry of compound **I** is given in Fig. 1.

The molecule has a planar geometry (with the exception of hydrogen atoms of methyl groups); the sum of the bond angles at C(1) and N(1) atoms was 360°.

One can pay attention to a shortened (2.586(2) Å) distance between the S(1)...O(1) atoms, which is significantly less than the sum of the van der Waals radii of the corresponding atoms (3.13 Å) and indicates that a specific interaction occurs between the sulfur and oxygen atoms (electrostatic attraction of oppositely charged sulfur and oxygen atoms) [6].

The similar interaction has previously been observed for 1-nitro-2-methylisourea (**II**) which is similar in the structure and reactivity in nucleophilic substitution reactions, with the S(1)...O(1) distances being 2.572(7)/2.572(9) Å [7]; and also for other compounds with the >C=NNO₂ nitrimine group directly bonded to the sulfur atom [8, 9]. At the same time, compound **II** had a potentially alternative conformational choice: the orientation of the nitro group to the amino group present in the molecule rather than to the sulfur atom, to form a hydrogen bond between one of the oxygen atoms of the nitro group and the amino group hydrogen. Such a conformation is typical of nitroguanidine derivatives and contributes to the maintenance of their planar geometry. However, the specific interaction with the sulfur atom, contrary to the data of quantum chemical calculations for a single molecule of compound **II**, was found to be more preferred in the crystal than the formation of the intramolecular hydrogen bond [7]. In compound **I** having two methylthio groups, there is no conformational alternative to the specific S...O interaction. Here, regardless of the availability of such an interaction for one of the methylthio groups, the lengths of both CH₃S–C(1) bonds in the molecule have close values (1.734(3) Å and 1.729(3) Å). This equalization of the lengths can be explained by the conjugation of atoms in the  molecular core of compound **I**, resulting in the electron

**Fig. 1.** Molecular structure of compound **I**.

density redistribution and equalization. The C(1)–S and C(1)–N(2) bond lengths are the evidence of such a conjugation. For comparison, the S–CH₃ bond lengths which do not have such a conjugation (1.790(3) Å and 1.792(3) Å) are much longer and are at the levels of the typical values of the single C–S bond in organosulfur compounds [10].

The C(1)–N(2) bond length (1.312(3) Å) is significantly shorter than the length of the similar bond in nitroguanidine derivatives (e.g. 1.372(2) Å for nitroguanidine [11]), and is shorter than that in compound **II** (1.339(5)/1.343(3) Å) [7]. At the same time, the value of the N(1)–N(2) bond length (1.395(3) Å) being typical of the single N–N bond [10], is much larger than that in nitroguanidine derivatives (1.334(2) Å for nitroguanidine [11]) and compound **II** (1.347(4)/1.351(3) Å) [7].

Thus, unlike nitroguanidine derivatives, for which the valence formulas do not reflect the real molecular structure of crystals [12], the molecular structure of compound **I** is within the traditional valence formulas, according to which the bond between the carbon and nitrogen atoms in the nitrimine group is double and it is single between the nitrogen atoms in >C=N–NO₂. This, in turn, points to the absence of the significant π electron delocalization in the nitrimine moiety, which is characteristic of nitroguanidine derivatives. As compared to the nitroguanidine derivatives, a greater separation of the nitro group in compound **I** affects the observed values of the N–O bond lengths. In compound **I**, these bond lengths are 1.218(2) Å and 1.222(2) Å (the greater value is observed for the bond in which the oxygen atom is additionally involved in the above mentioned intramolecular interaction with the sulfur atom). Meanwhile, for example, for nitroguanidine in which the nitro group is involved in the conjugation with the guanidine moiety of the molecule, the lengths of the similar bonds are 1.238(2) Å and 1.247(2) Å (the bond in which the oxygen atom additionally participates in the formation of the intramolecular hydrogen bond has the greater value). In the absence of the through conjugation between the nitro group and imidodithiocarbonate molecular moiety in compound **I**, the high planarity of the molecule is due to the intramolecular specific S...O interaction hindering the rotation of the nitro group.

However, the analysis of the distances between the atoms of different molecules in the crystal lattice has not revealed any significant intramolecular interactions in the molecular packing in the crystal of compound **I**. The properties of the substance itself such as a relatively low melting point (65°C) indicating a low energy of the crystal lattice, gives evidence of the absence of such interactions.

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