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Single crystal X-ray structure of (Z)-1-bromo-1-nitro-2-phenylethene

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ABSTRACT

The title compound - (Z)-1-bromo-1-nitro-2-phenylethene - was prepared by a three-step reaction. Its structure was confirmed by spectral analysis as well as X-ray crystallography. It was found, that the compound crystallized in the orthorhombic system, space group *Pbca*, $a=11.5296(6)\text{\AA}$, $b=7.5013(5)\text{\AA}$, $c=19.7187(12)\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$, $Z=8$.

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1. Introduction

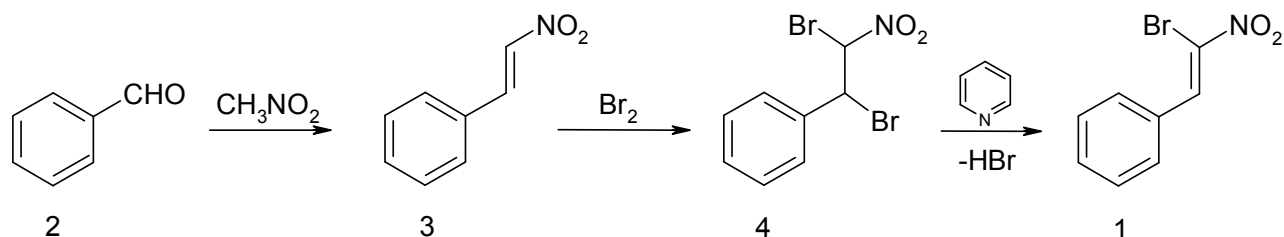
The present work is part of our project on synthesis, structure investigation and property evaluation of conjugated nitroalkenes^{1,2,3}. In particular, we decided to shed light on structure of 1-bromo-1-nitro-2-phenylethene. This compound is known⁴, but – unfortunately – complete structural data are not available. In the other hand, title compound is very important from practical point of view. Gem-halonitro functionalized compounds have significant antibacterial activity and the ability to stimulate cell sensitivity and inhibit tissue bleeding processes⁵. Many β -arylnitroethenes and their derivatives have been documented to display diverse biological activities including antibacterial⁶, molluscicidal^{7,8} and anticancer^{9,10,11}. β -arylnitroethenes are also used as versatile intermediates in organic syntheses such as selective reductions to diverse functional groups, the Diels-Alder cycloaddition reactions^{12,13}, and the Michael addition¹⁴.

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2. Results and Discussion

For the preparation of β -nitrostyrenes halosubstituted in the β -position we can use of three procedures: (I) via interaction between nitril halogenides and alkenes, (II) condensation of gem-halonitrocompounds with aldehydes¹⁵, or (III) via addition of halogenide to the nitrostyrene, with subsequent elimination of hydrogen halide from the halonitro compound⁴. We decided on last strategy (Scheme 1) (see experimental section).



Scheme 1.

2.1 Crystal structure determination of **1**

The crystal structure of **1** is shown in Fig. 1. Experimental diffraction data were collected on a KM4CCD kappa-geometry diffractometer, equipped with a Sapphire2 CCD detector. An enhanced X-ray MoK α radiation source with a graphite monochromator was used. Determination of the unit cells and data collection were carried out at 298 K. Data reduction, absorption correction and space group determination were made using the CRYCALISPRO software package¹⁶. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXL program package¹⁷.

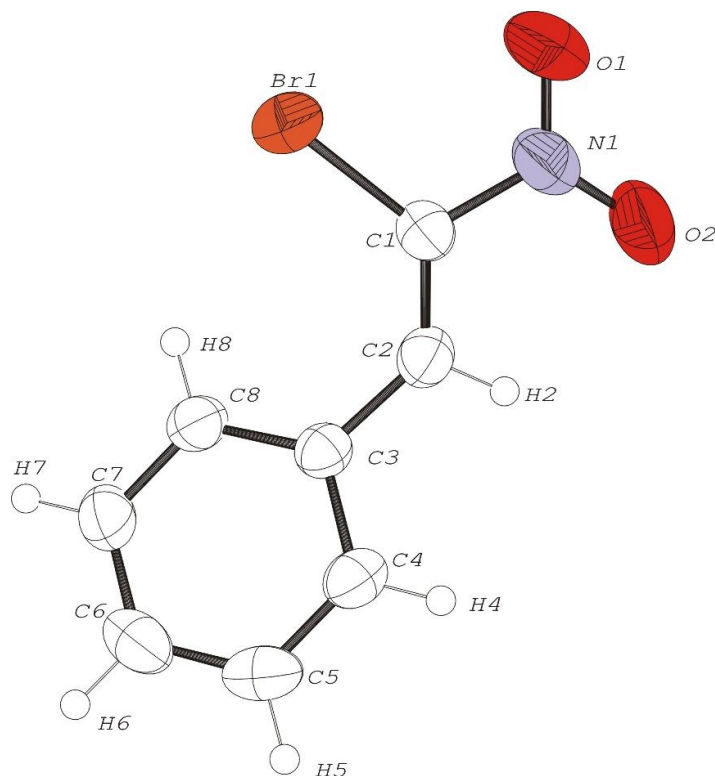


Fig 1. Molecular structure of **1**

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-1030430). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/perl/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

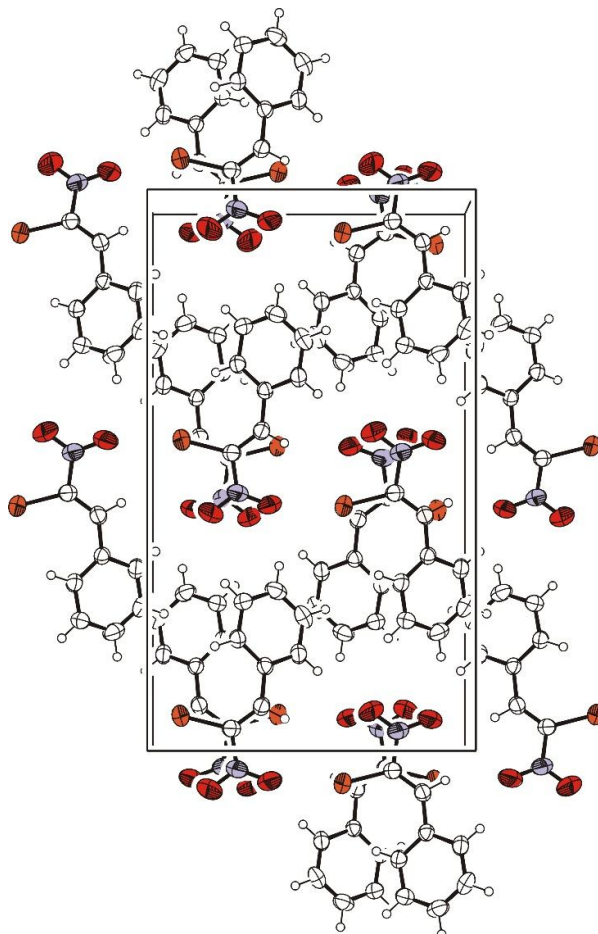


Fig 2. Crystal packing of **1**

2.2 Description of the crystal structure of **1**

The crystal structure of **1** ($C_8H_6BrNO_2$) and its crystal packing are shown in Fig. 1 and Fig. 2, respectively. The selected crystallographic data and experimental details for **1** are given in Table 1, selected bond lengths and angles for this compound are shown in Table 2. Initially we decided to shed light on configuration of **1**. Unfortunately, determination of the geometric isomerism of **1** by the NMR spectra is practically impossible due to lack of diagnostic protons. This problem has been successfully resolved by the X-ray crystallography. It was found, that the phenyl group and bromine are on the same side of $C1=C2$ double bond, whereas the nitro group and hydrogen atom H1 are on the another side. Thus, the molecule has a *Z* configuration. We determined that the dihedral angle between the 1-bromoethylene moiety and the nitro group (T1) is equal to 3.00° , whereas the dihedral angle between phenyl and 1-bromoethene moieties (T2) is equal to 28.67° . Therefore the molecule is not planar. In *p*-dimethylamino- β,β -bromonitrostyrene¹⁸, the closest structurally compound, the T2 angle is equal to 4.81° . It should be noted also that C1-C2 bond lengths in ethene moiety is equal to $1.332(5)$ Å and shows typical double-bond character. The crystal structure of **1** shows a weak intermolecular interaction between O2 atom of one molecule and H2 and H6 atoms of the two other molecules.

Table 1. Crystal Data and Experimental Details for **1**

Empirical formula	C ₈ H ₆ BrNO ₂	Scan type	ω -2 θ
Formula weight	228.045	θ range	2.71 – 28.36
Crystal color	yellow	Index range	-14 \leq h \leq 13 -9 \leq k \leq 7 -24 \leq l \leq 19
Crystal system	Orthorhombic	Measured reflections	2828
Space group	<i>Pbca</i>	Independent reflections	1678
Z	8	Observed refl. $I \geq 2\sigma(I)$	1195
V, Å ³	1705.41(18)	Completeness to $\theta = 28.36^\circ$	99.9
D (calc), g.cm ⁻³	1.776	Refinement on	F^2
a, Å	11.5296(6)	Final <i>R</i> indices [$I > 2\sigma(I)$]	3.12
b, Å	7.5013(5)	R (all data)	5.22
c, Å	19.7187(12)	The goodness of fit on F^2	1.016
α, β, γ , deg	90	Weighting parameter a/b	0.047/0.866
μ , mm ⁻¹	4.776	Max and min $\Delta\rho$ (e Å ⁻³)	0.321/-0.413
F(000)	869		

Table 2. Selected Bond Lengths and Angles (Å, °) of **1**

Bond	d	Angles	ω
C4 C5	1.378(5)	O1 N1 O2	122.1(4)
C3 C4	1.402(5)	O1 N1 C1	119.0(3)
C8 C3	1.399(5)	O2 N1 C1	118.9(3)
C7 C8	1.378(4)	N1 C1 C2	118.7(3)
C6 C7	1.376(5)	N1 C1 Br1	113.3(2)
C5 C6	1.377(5)	Br1 C1 C2	128.1(3)
C2 C3	1.459(4)	C2 C3 C4	131.5(3)
C1 C2	1.332(5)	C2 C3 C8	124.5(3)
C1 Br1	1.866(3)	C4 C3 C8	117.8(3)
C1 N1	1.479(4)	C3 C4 C5	121.2(3)
N1 O1	1.209(5)	C4 C5 C6	119.7(3)
N1 O2	1.229(5)	C5 C6 C7	120.3(3)
		C6 C7 C8	120.3(3)
		C7 C8 C3	120.7(3)

4. Experimental

4.1. Materials and Methods

¹H NMR spectra were recorded with a Bruker Avance AMX (300MHz). The spectra were measured in CDCl₃ using TMS as the internal standard. Melting point was determined on a Boetius apparatus. Infrared spectra was determined on a Bio-Rad 175 C spectrometer, using KBr disks. Elemental analysis was performed on a Perkin-Elmer PE-2400 CHN apparatus. All starting materials, reagents and solvents were purchased from commercial sources. Condensation between benzaldehyde and nitromethane as well as addition of bromine to double bond of β -nitrostyrene were proceed according to known procedure^{4,19}.

4.2. Preparation of 1 (*Z*)-1-bromo-1-nitro-2-phenylethene

For preparation of **1** in a flask equipped with condenser and dropping funnel placed 84g 1,2-dibromo-1-nitro-2-phenylethene and 340ml of cyclohexane. Mixture was stirred and heated to the reflux solution of 25ml pyridine in 75ml cyclohexane was slowly added. Heating was continued by 15 min. The mixture was washed with ether (400ml) and water (100ml). Organic layer was washed with

diluted hydrochloric acid and water, and then dried over Na₂SO₄. Solution was concentrated and cooled. The crude product was separated by filtration and recrystallized from glacial acetic acid and than cyclohexane. The yellow needles (37g, 82 %) were obtained.

4.3 Physical and Spectral Data

(Z)-1-bromo-1-nitro-2-phenylethene: mp 64-66°C (reported: 67-68°C⁴, 63-64°C²⁰). Anal. Calc. for C₈H₆BrNO₂: C, 42.14; H, 2.65; N, 6.14. Found: C, 42.27; H, 2.41; N, 6.18. ¹H-NMR δ (ppm) 7.46-7.58 (3H, m), 7.83-7.95(2H, m), 8.63(1H, s); IR (KBr, cm⁻¹) 3033 (m), 1598 (m), 1530 (s), 1446 (m), 1309 (s), 1285 (s), 1210 (m), 957 (s), 930 (s), 764 (s), 689 (m), 503 (m);

3. Conclusions

In conclusion, single crystal x-ray structural analysis proved without any doubts geometrical Z-configuration of 1-bromo-1-nitro-2-phenylethene. However, surprisingly molecule of this compound is not planar.

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