Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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To cite this Article Mloston, Grzegorz , Depczynski, Robert , Woznicka, Marta , Laur, Peter , Englert, Ulli , Hu, Chunhua and Heimgartner, Heinz(2005) 'Sulfur addition to aldimines: thioamides, not thiaziridines, as products; revision of an old report', Journal of Sulfur Chemistry, 26: 2, 111 — 117
To link to this Article: DOI: 10.1080/17415990500056788
URL: http://dx.doi.org/10.1080/17415990500056788

Journal of Sulfur Chemistry
Vol. 26, No. 2, April 2005, 111–119

Taylor & Francis
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RESEARCH ARTICLE

Sulfur addition to aldimines: thioamides, not thiaziridines, as products; revision of an old report

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(Received 3 December 2004; in final form 17 January 2005)

Dedicated to Professor Rolf Huisgen, Ludwig-Maximilians-Universität München, Germany, on the occasion of his 85th birthday.

The reaction of 4-(phenylimino)butan-2-ol with ammonium polysulfide in refluxing EtOH yields 3-hydroxy-*N*-phenylbutanethioamide as the only isolated product. The structure has been established by single-crystal X-ray diffraction. Treatment of *N*-benzylidenamines with ammonium polysulfide has proven a general method for the preparation of thiobenzamides.

Keywords: Azomethines; Sulfur transfer; Thiaziridines; Thioamides

1. Introduction

Sulfur-containing saturated three-membered heterocycles are compounds with significant importance not only in organic synthesis but also for theoretical and spectroscopic studies [1–6]. Of these, only thiiranes are well known, fully characterized, and frequently used materials [1]. Among the derivatives with two heteroatoms in the three-membered ring, some dithiiranes have been prepared, isolated, and characterized recently [7], whereas oxathiiranes are sometimes involved as intermediates in desulfurization processes of sulfines (thiocarbonyl *S*-oxides) [8]. Similarly, thiaziridines have been postulated as intermediates in transformations of thiocarbonyl *S*-imides into imines [9–11].

In our recent studies on reactions of thiocarbonyl compounds with organic azides, thiaziridines were proposed as key intermediates in the sulfur-transfer process leading to the

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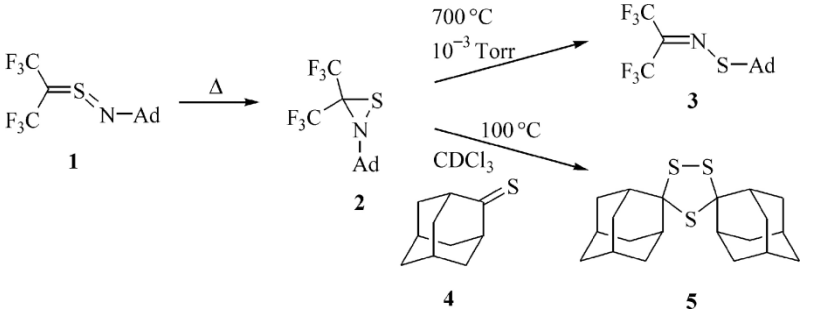
‡Part of the diploma thesis of R.D., University of Lodz, 2000; presented at the ICHAC-6, Lodz, 2001.

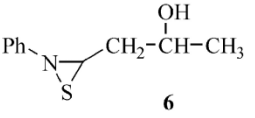
Journal of Sulfur Chemistry
ISSN 1741-5993 print/ISSN 1741-6000 online
http://www.tandf.co.uk/journals
DOI: 10.1080/17415990500056788

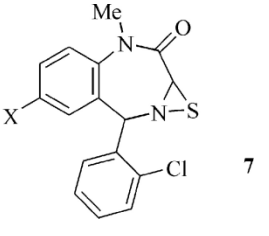
in situ formation of thiocarbonyl *S*-sulfides, which further react to give 1,2,4-trithiolanes [12]. As a possible precursor of a thiaziridine, the stable thiocarbonyl *S*-imide **1** was thermolyzed under flash vacuum pyrolysis (FVP) conditions. The only product isolated was the rearranged compound **3** [13] (scheme 1). Thiaziridine **2** was postulated as the intermediate, which in the gas phase undergoes a conversion into **3** without elimination of sulfur. On the other hand, heating of **1** in $CDCl_3$ in the presence of adamantanethione **4** led to the known 1,2,4-trithiolane **5** [14, 15]. In accord with the proposed sulfur-transfer reactions [12], thiaziridine **2** is believed to act as the S-donor, which transforms **4** into the corresponding thiocarbonyl *S*-sulfide. The latter undergoes a [3 + 2] cycloaddition with **4** to give **5**.



SCHEME 1

To the best of our knowledge, there exist only two reports in which isolated reaction products are formulated as thiaziridines [16, 17].† In one of them, published in 1896, the treatment of 4-(phenylimino)butan-2-ol ('Aldolanilin') with ammonium polysulfide ('Schwefelammon')‡ in EtOH was described as a method for the preparation of thiaziridine **6** [16]. More than 70 years later, thiaziridine structures of type **7** were included into the Beilstein Database as patented benzodiazepine derivatives [17].





Owing to our current interest in reactions involving thiaziridines as intermediates, we decided to repeat the experiment reported by v. Miller and Plöchl [16] with the aim of proving unequivocally the structure of the crystalline reaction product, whose identity so far rests on its elemental composition only.

†Thiaziridine 1,1-dioxides with bulky substituents are known as isolable compounds [2, 18].

‡'Schwefelammon' means literally NH_4HS and $(NH_4)_2S$; the sulfidation reactions described [16] leave no doubt, however, that the rather unstable compound NH_4HS has become oxidized to the polysulfide, at least partly, before or during the reaction, fortuitously or on purpose.

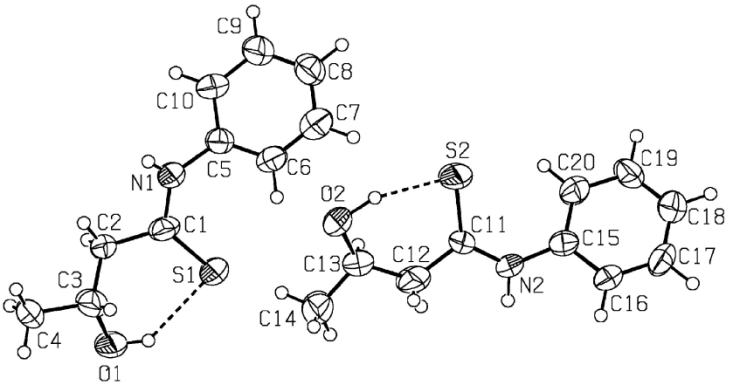


Figure 1. Displacement ellipsoid plot (50% probability) [21] of one of the two symmetrically independent molecules of **9.**

2. Results and discussion

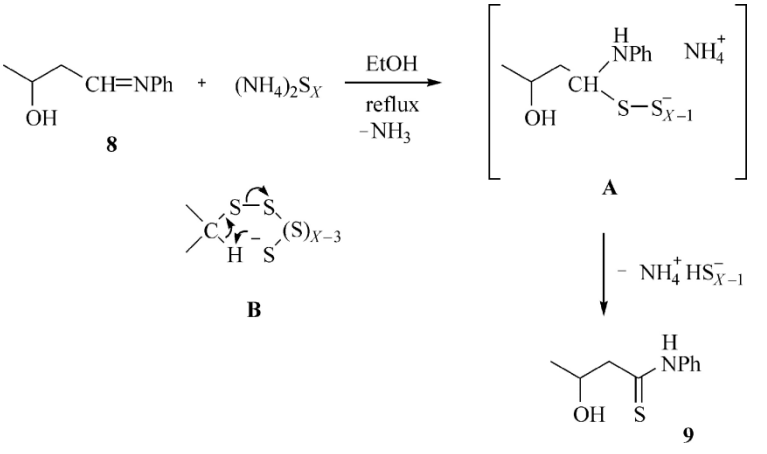
The imine **8** [19] is an unstable compound (*cf.* ref. [16]) and was used as starting material for the reaction with freshly prepared ammonium polysulfide, $(NH_4)_2S_x$, without further purification. Heating of a mixture of **8** and excess of $(NH_4)_2S_x$ in EtOH under reflux for 5 min led to a viscous orange oil, which was purified by column chromatography. Besides elemental sulfur, only one organic product was isolated, and this was recrystallized from petroleum ether/Et_2O to give almost colourless crystals. The melting point and elemental analysis were in accord with the data reported by v. Miller and Plöchl [16]. In the ^{1}H NMR spectrum ($CDCl_3$), two broad signals at δ 3.16 and 9.72 ppm for OH and NH showed that the structure differs from that of compound **6**. The ^{13}C NMR spectrum revealed two sets of signals (ratio ~10:1) corresponding to the structures of two rotamers of thioamide **9**[†] with the characteristic C=S resonance at δ_c 202.4 ppm. Finally, the structure of **9** was established by single-crystal X-ray analysis (figure 1). Thus, the substance described in ref. [16] as thiaziridine **6** is actually the β-hydroxythioamide **9**. This class of compounds has been only rarely described [22].

The asymmetric unit contains two molecules of very similar conformations. In addition to intramolecular hydrogen bonds between the sulfur and oxygen atom [distance O . . . S 3.047(4) and 3.062(4) Å, resp.], intermolecular hydrogen bonds between NH and the O-atom link neighbouring molecules to chains along the [100] direction.

A possible explanation of the reaction pathway leading to **9** is shown in scheme 2. The first step is a nucleophilic addition of the polysulfide anion to the imino group of **8** to give an ion-pair **A**. Then, the thioamide **9** is formed by elimination of ammonium hydropolysulfide. For this elimination, a cyclic transition state of type **B** is likely.

It has been shown that differently substituted aldimines can be converted into thioamides by treatment with elemental sulfur. In all cases reported, a high temperature (100–260 °C) is required to perform the reaction [23]. In some cases, mixtures of sulfur and H_2S were applied without heating [24]. However, reports on reactions of imines with $(NH_4)_2S_x$ aimed at the preparation of thioamides are not known. Therefore, reactions of aldimines **10a–c** with ammonium polysulfide were carried out in our laboratories. The transformations occurred smoothly in MeOH at room temperature (1 h) to give the expected thioamides **11a–c**, albeit in moderate yields of less than 50% (scheme 3). On the other hand, this protocol was inefficient in the case of *N*-(benzylidene)aniline (**10d**, R = Ph).

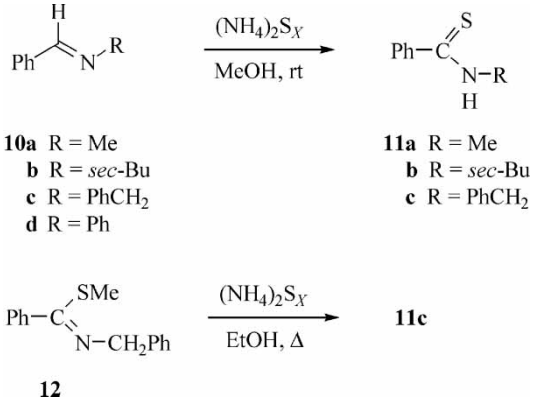
[†]The doubling of the signals results from the presence of two rotamers (*cf.* ref. [20]).



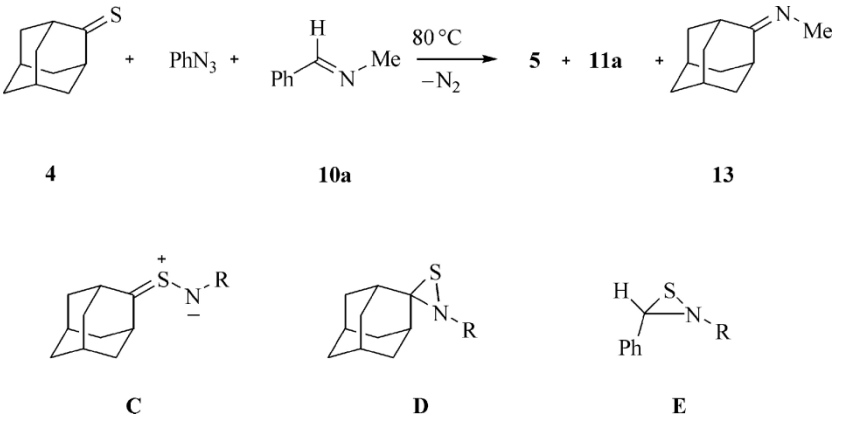
SCHEME 2

As an additional experiment, thiobenzimidate **12** was treated with $(NH_4)_2S_x$ in boiling EtOH. The reaction proceeded by formal elimination of MeSH, and thioamide **11c** was isolated in 45% yield. A convincing mechanism for this reaction cannot be presented yet.

The formation of 1,2,4-trithiolanes of type **5** in the reactions of thioketones with organic azides was rationalized by sulfur-transfer processes, which are initiated by transient thiocarbonyl *S*-imides **C** (scheme 4). Ring closure leads to unstable thiaziridine derivatives of type **D**, which act as sulfur donors [12]. With the aim of examining the ability of aldimines to behave as sulfur acceptors in this system, a three-component reaction using **4**, phenyl azide, and **10a** was carried out at 80 °C. ^{1}H NMR analysis of the crude product indicated the presence of **11a**, which was subsequently isolated after chromatographic work-up along with comparable amounts of **5** (scheme 4). As mentioned in our previous report [12], isolation of the imine **13** is not possible under these conditions. The formation of **11a** is strong evidence that aldimines **10** are reactive sulfur acceptors, and that thiaziridines of type **E**, *i.e.* derivatives of aldimines, are likely intermediates that undergo an intramolecular stabilization *via* ring opening and H-shift. In contrast, thiaziridines of type **D**, derived from ketimines, are subjected to a sulfur extrusion. Similar rearrangements of oxaziridines, generated thermally or photochemically



SCHEME 3



SCHEME 4

from aldonitrones or heterocyclic *N*-oxides or obtained by oxidation of the imine precursors, leading to carboxamides are well documented [25].

3. Conclusions

Our study shows that the product of the reaction of **8** and $(NH_4)_2S_x$ described in ref. [16] is neither the thiaziridine **6** nor the isomeric thionitrone but the thioamide **9**. As proposed in scheme 2, the formation of **9** does not require a thiaziridine as an intermediate. However, the intermediacy of such species cannot be excluded in the reactions with elemental sulfur, in analogy to oxidation of imines leading to oxaziridines [26]. In the light of the presented results, the thiaziridine structures of type **7** are also questionable.

The synthesis of thioamides from easily available aldimines and $(NH_4)_2S_x$ supplements known procedures for the preparation of this important class of organic compounds (*cf.* ref. [27]). In spite of the fact that the formation of thioamides in three-component reactions (scheme 4) is not important from the preparative point of view, this is the first evidence that aldimines are sulfur acceptors, which efficiently compete with thioketones in this reaction.

4. Experimental

4.1 *General*

Mps were determined in capillaries on a Melt-Temp II apparatus (Aldrich) and are not corrected. IR spectra were registered with a NEXUS FT-IR spectrophotometer (samples in KBr). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Tesla BS567A (80 and 20 MHz, respectively) or Varian Gemini 200-BB (^{1}H, 200 MHz) instrument. *J*-Values are given in Hz. The multiplicity of the ^{13}C signals was deduced from DEPT spectra. Elemental analyses were performed by the Microanalytical Laboratory of the Polish Academy of Sciences in Lodz.

4.2 *Starting materials*

3-Hydroxybutanal was prepared from acetaldehyde in the presence of 10% aq. NaOH according to a known procedure [28]. The preparation of the corresponding phenylimine **8** was

carried out following the method described by v. Miller and Plöchl [16]. The crude product, which precipitated from Et_2O solution after addition of small amounts of hexane, separated as an orange semi-solid and was used for the reaction with $(NH_4)_2S_x$ without further purification. Attempted distillation of **8** *in vacuo* as well as column chromatography led to complete decomposition. *N*-(3-Hydroxybutylidene)aniline **8**: Almost quantitative yield (crude material, unstable). ^{1}H NMR (80 MHz) δ 0.58–2.17 (m, 6 H); 4.83 (d, OH); 6.33–6.93 (m, 3 arom. H); 6.97–7.32 (m, 2 arom. H); 7.33 (s, CH=N).

N-Benzylidenemethylamine **10a** [29], *N*-benzylidene(1-methylpropyl)amine **10b** [30], and *N*-benzylidenebenzylamine **10c** [31] were prepared according to known procedures from the corresponding amine and benzaldehyde. Pellets of KOH were added to improve separation of the organic and aqueous layers. Pure products were obtained by distillation *in vacuo*. *S*-Methyl *N*-(benzyl)thiobenzimidate **12** was prepared from methyl dithiobenzoate and benzyl azide according to ref. [32]. Ammonium polysulfide, $(NH_4)_2S_x$, was obtained from NH_3, H_2S, and elemental sulfur following the protocol in ref. [33]. The red-orange crystals were stored in EtOH solution in the refrigerator. Immediately before use, an aliquot was filtered off and washed with Et_2O.

4.3 *Reaction of* 8 *with* $(NH_4)_2S_x$

A solution of **8** (2.02 g, 12 mmol) in abs. EtOH (5 ml) was treated with an excess of freshly filtered $(NH_4)_2S_x$ (2.36 g), the mixture was heated to reflux for 5 min, and EtOH was evaporated off. The solid residue was treated with Et_2O (20 ml), and elemental sulfur was separated by filtration. The clear Et_2O solution was diluted with small portions of petroleum ether until a colourless precipitate appeared. The solid was filtered off and the solution was stored in the refrigerator. After several hours a crystalline product had formed, and this was filtered off. The mother liquor was again stored in the refrigerator to give another crop of crystals, which was combined with the first portion. Analytically pure thioamide **9** was obtained after recrystallization from MeOH.

3-Hydroxy-*N*-phenylbutanethioamide **9**. Yield 435 mg (18%). Mp 92–93 °C (ref. [16]: 92 °C). IR (KBr) ν3000–2800*vs* (br, OH), 1597*m*, 1559*m*, 1497*s*, 1414*vs* (br), 1311*s*, 1207*s*, 1146*s*, 767*s*, 715*vs*, 691*s*. ^{1}H NMR [200 MHz; major rotamer (85%)] δ 1.32 (d, J = 6.3, Me), 2.87 (dd, J = 15.1, 8.5, H_B of CH_2), 3.03 (dd, J = 15.1, 2.6, H_A of CH_2), 3.16 (br d, J = ~3.3, OH), 4.00–4.55 (m, CH), 7.25–7.75 (m, 5 arom. H), 9.72 (br s, NH). The ratio of the rotamers (85:15) was estimated from the intensities of the Me signals at δ 1.32 (major) and 1.55 ppm (minor). ^{13}C NMR δ 23.0 (q, Me), 55.5 (t, CH_2), 67.1 (d, CH), 124.2, 127.2, 129.2 (3 d, 5 arom. CH), 139.0 (s, arom. C), 202.4 (s, C=S). Signals of the minor rotamer (15%) were found at δ 22.3, 48.0, 66.4, 126.0, 128.7, 130.1, 137.8, and 205.0. [Calc. for $C_{10}H_{13}NOS$ (195.28): C, 61.51; H, 6.71; N, 7.17; S, 16.42. Found: C, 61.30; H, 6.89; N, 7.24; S, 16.50%] (ref. [16] Found: C, 61.52; H, 6.92; N, 7.32; S, 16.36%).

In another experiment, the Et_2O solution obtained after separation of the coloured, oily by-products was evaporated and the residue was purified by column chromatography (SiO_2) using petroleum ether with increasing amounts of dichloromethane as the eluent. Crude thioamide **9** was obtained as the main fraction (660 mg, 27%) and purified by crystallization from petroleum ether containing small amounts of dichloromethane.

4.4 *Reactions of imines* 10a–c *with* $(NH_4)_2S_x$

4.4.1 General procedure. A mixture of an imine **10a**–**c** (10 mmol) and freshly filtered $(NH_4)_2S_x$ (2.0 g) in MeOH (10 ml) was stirred at room temperature. After 1 h, MeOH was

evaporated off and the semi-solid residue was triturated with 20 ml of Et_2O. The precipitated sulfur was filtered off, and, after evaporation of the solvent, the crude thioamide **11a–c** was crystallized from MeOH.

N-(Methyl)thiobenzamide **11a**. Yield 634 mg (42%). Mp 75–76 °C (ref. [34]: 77–79 °C). ^{13}C NMR δ 200.4 (s, C=S) (ref. [34]: 200.0).

N-(1-Methylpropyl)thiobenzamide **11b**. Yield 929 mg (48%). Mp 42–43.5 °C (ref. [35]: 47–48 °C). ^{13}C NMR δ 10.4, 18.9 (2 q, 2 Me), 28.7 (t, CH_2), 53.6 (d, CH), 127.0, 128.6, 131.1 (3 d, 5 arom. CH), 142.6 (s, 1 arom. C), 198.6 (s, C=S).

N-(Benzyl)thiobenzamide **11c**.[†] Yield 976 mg (43%). Mp 87–88 °C (ref. [35]: 85–87 °C). ^{13}C NMR δ 199.7 (s, C=S) (ref. [34]: 199.3).

4.5 *Three-component reaction with* N-*benzylidenemethylamine* **10a**, *adamantanethione* **4**, *and phenyl azide*

Thioketone **4** (166 mg, 1 mmol) and **10a** (238 mg, 2 mmol) were dissolved in 0.5 ml of phenyl azide, and the magnetically stirred orange solution was heated at 80 °C. The evolution of nitrogen was monitored by means of a gas burette connected to the reaction flask. When the gas evolution ceased, the crude mixture was analyzed by ^{1}H NMR and the ratio of *N*-(methyl)thiobenzamide **11a** and *N*-(benzylidene)methylamine **10a** was determined to be ~1:3. The volatile components were removed by distillation in an oil-pump vacuum and the residual thick oil was separated on preparative TLC plates coated with SiO_2 (eluent: dichloromethane). *N*-(Methyl)thiobenzamide **11a** was recrystallized from benzene. Yield 40 mg (26%). ^{1}H NMR and IR spectra were identical with those of an original sample. Trithiolane **5** was isolated as a less polar fraction and was recrystallized from MeOH. Yield 106 mg (29%). ^{1}H NMR and IR spectra were identical with those of an original sample (ref. [12]).

4.6 *X-Ray crystal-structure determination of* **9** *(see table* **1** *and fig.* **1**)[‡]

A crystal was mounted on a glass fibre for geometry- and intensity-data collection with a Bruker SMART Apex CCD area detector on a D8 goniometer. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. All data were collected using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,73$ Å) with the ω scan method [37] and processed with the SAINT+ program [38]. The structure was solved by direct methods and refined using SHELXTL [39]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C−H = 0.98 Å) and included as riding with $U_{iso}(H) = 1.3\,U_{eq}$(non-H). Hydrogen atoms bonded to nitrogen or sulfur atoms were located from difference Fourier maps and refined freely and isotropically. Anomalous dispersion effects were sufficient to determine the polarity of the individual crystal in the non-centrosymmetric space group $Pna2_1$; an enantiomorph polarity parameter [40] of 0.01(16) was obtained. Crystal data, data collection parameters, and refinement results are listed in table 1, and a view of the molecule is shown in figure 1.

[†]Compound **11c** was also obtained in 45% yield after treatment of methyl *N*-(benzyl)thiobenzimidate [36] with $(NH_4)_2S_x$. The reaction was carried out in refluxing EtOH; reaction time 1 h.

[‡]CCDC-247195 contains supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal data, data collection parameters, and convergence results for compound **9**.

Empirical formula	$C_{10}H_{13}NOS$
Formula weight	195.27
Crystal system	Orthorhombic
Space group	$Pna2_1$
Radiation (λ [Å])	Mo-K_α (0.710 73)
a [Å]	11.1385(13)
b [Å]	11.9536(14)
c [Å]	15.6527(19)
V [Å^3]	2084.1(4)
Z	8
D_{calc} [g/cm^3]	1.245
$F(000)$	832
μ [mm^{-1}]	0.271
θ range [deg]	2.1–28.4
Completeness of data	0.997
Temperature [T/K]	293
Crystal size [mm]	$0.63 \times 0.13 \times 0.10$
Reflections collected	26 575
R_{int}	0.103
Reflections unique	2702
Reflections unique observed $I > 2\sigma(I)$	1368
Variables	251
R_1 (obs. data, all data)	0.0574, 0.1210
wR_2 (obs. data, all data)	0.1331, 0.1552
GOF	0.896
Max. residual electron density [e/Å^3]	$+0.353/-0.183$

Acknowledgements

We thank the analytical services of our institutes for spectra and analyses, and the Polish State Committee for Scientific Research (Grant No. 4 T09A 046 25) and F. Hoffmann-La Roche AG, Basel, for financial support.

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