Synthesis of 1,2-bis(1-boraadamant-2-yl)ethane derivatives. Crystal structure of the racemic form

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Condensation of triallylborane with octa-1,7-diyne followed by treatment of the reaction mixture with methanol afforded a mixture of stereoisomeric 1,4-bis(3-methoxy-3-borabicyclo[3.3.1]non-6-en-7-yl)butanes (**1a,b**). Hydroboration of the latter with a solution of BH_3 in THF yielded the tetrahydrofuran complex of 1,2-bis(1-boraadamant-2-yl)ethane (**2**) as a mixture of diastereomers. Pure racemate (**2a**) was obtained by crystallization from the reaction mixture and it was converted into the pyridine complex of 1,2-bis(1-boraadamant-2-yl)ethane (**3**). The structure of the latter was established by X-ray diffraction analysis. Complex **2a** was converted into the corresponding racemic 1,2-bis(1-hydroxyadamant-2-yl)ethane (**4a**) by the carbonylation-oxidation reaction.

Key words: triallylborane, 1-boraadamantane compounds, 1,2-bis(1-boraadamant-2-yl)ethane, hydroboration, coordination complexes of bis-organoboranes, X-ray diffraction analysis.

1-Boraadamantane and its derivatives are excellent starting compounds for preparing various adamantane, azaadamantane, bicyclic, and cyclohexane compounds,[1—3] many of which are either difficultly accessible or cannot be prepared according to classical procedures. The general procedure for the synthesis of 1-boraadamantanes involves hydroboration-isomerization of 7-substituted 3-methoxy-3-borabicyclo[3.3.1]non-6-enes, which are prepared upon treatment of products of allylboron-acetylenic condensation (ABAC) with MeOH, *viz.*, by thermal reactions (120—140 °C) of terminal acetylenes with triallyl- or trimetallylborane.[1—3] This procedure makes it possible to prepare virtually any 2-mono- or 2,2-dialkyl derivatives of 1-boraadamantane as well as their analogs containing functional groups in the side chain.[4] It was of interest to extend the scope of this synthetic procedure as well as to estimate the fields of application of ABAC products in the synthesis of new polyhedral systems containing two 1-boraadamantane cores in the molecule. In the present work, we report the synthesis of two adducts of 1,2-bis(1-boraadamantan-2-yl)ethane and conversions of their diastereomeric complexes with tetrahydrofuran into the corresponding 1-adamantanols (see the previous publication[5]). The structural parameters of the racemic form of the bis-pyridine complex are discussed.

Heating of triallylborane with octa-1,7-diyne at 135—140 °C followed by treatment of the reaction mixture with MeOH afforded 1,4-bis(3-methoxy-3-borabicyclo[3.3.1]non-6-en-7-yl)butane (**1**) as a 1 : 1 mixture of diastereomers, *viz.*, of the racemate (**1a**) and the *meso* form (**1b**) (Scheme 1). Hydroboration of compound **1** with a solution of $BH_3 \cdot THF$ in THF followed by heating (66 °C, 2 h) gave the tetrahydrofuran complex of 1,2-bis(1-boraadamantan-2-yl)ethane (**2**), which is the first compound containing two 1-boraadamantane fragments in the molecule. The ^{13}C NMR spectrum of complex **2** has two sets of signals corresponding to the racemate (**2a**) and the *meso* form (**2b**) (Table 1). The individual racemic diastereomer **2a** was crystallized from the reaction mixture when tetrahydrofuran was partially distilled off. Using this procedure, we succeeded in isolating racemate **2a** in 45% yield. Adducts **2a** and **2b** are very readily oxidized in air.

Treatment of adduct **2a** with pyridine afforded air-stable bis-pyridine complex **3**. The configuration of the latter was established by X-ray diffraction analysis.

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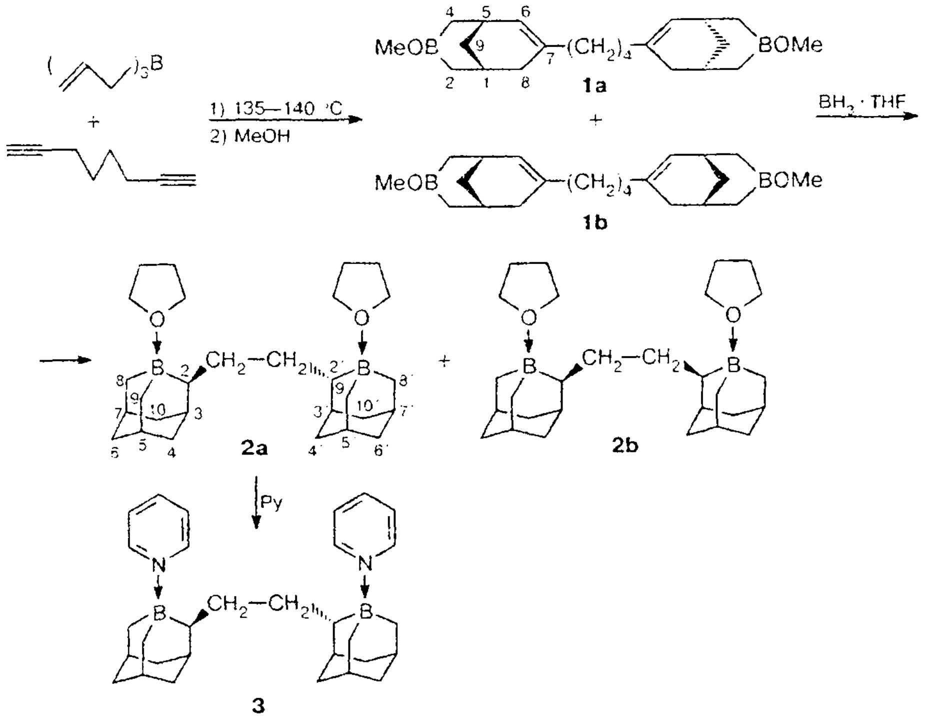
Table 1. Chemical shifts in the ^{13}C NMR spectra of the 1,2-bis(1-boraadamantan-2-yl)ethane complexes

Compound	Solvent	C(2)	C(8)	C(9)	C(3)	C(4)	C(5)	C(7)	C(6)	C(10)	Other signals
2a	THF-d_8	40.0	28.8	26.6	36.8	34.3	34.7	34.5	41.5	42.2	THF, 68.3, 26.0; CH_2, 30.0
2b	THF-d_8	38.7	28.8	26.9	36.0	34.1	34.7	34.4	41.5	42.2	THF, 68.3, 26.0; CH_2, 28.2
3	Py-d_5	41.0	35.8	26.9	36.1	34.6	33.8	33.2	41.6	42.65	CH_2, 30.3; Py, 125.6, 139.4, 145.0

Scheme 1*



The structure of molecule **3** is shown in Fig. 1. The crystal structure consists of a racemic mixture of separated LL and DD molecules. The molecule has a transoid structure. The 1-boraadamantyl fragments are located on opposite sides of the central C(1)—C(2) bond. The C(2')—C(1)—C(2)—C(2") torsion angle is 167.0°. The B—N bonds are virtually parallel to the central C(1)—C(2) bond. The C(1)—C(2) bond forms angles of 8.4 and 13.8° with the B(1')—N(1') and B(1")—N(1") bonds, respectively.

The configurations of the asymmetrical centers in both halves of the molecule (the C(2') and C(2") atoms) are identical. The environments about the asymmetrical atoms, *viz.*, the projections along the C(2')—H(2'A) and C(2")—H(2"A) bonds, are shown in Fig. 2.

The pyridine rings are in identical orientations with respect to the 1-boraadamantyl fragments. The plane of the ring virtually coincides with the bisecting BC(9)C(5)C(10) plane. The dihedral angles between the planes, N(1')C(11')C(15')/B(1')C(9')C(5')C(10') and N(1")C(11")C(15")/B(1")C(9")C(5")C(10"), are 5.3° and 4.5°, respectively. The orientations of the pyridine rings with respect to the adjacent 1-boraadamantyl fragments are also identical, *viz.*, the plane of the Py' ring is approximately coplanar with the mean plane of the B(1")C(2")C(3")C(4")C(5")C(9") ring (more precisely, with the plane of the "chair base" of this ring) and, on the contrary, the plane of the Py" ring is virtually coplanar with the mean B(1')C(2')C(3')C(4')C(5')C(9') plane (the plane of the "chair base" of this ring). The N(1')C(11')C(15')/C(2")C(3")C(5")C(9") and N(1")C(11")C(15")/C(2')C(3')C(5')C(9') dihedral angles are 20.7 and 15.8°, respectively. The geometric parameters of the pyridine rings have standard values.

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* Hereinafter, the structures of one enantiomer of the compounds are shown in the schemes for simplicity. Actually, all chiral compounds occur as racemates.

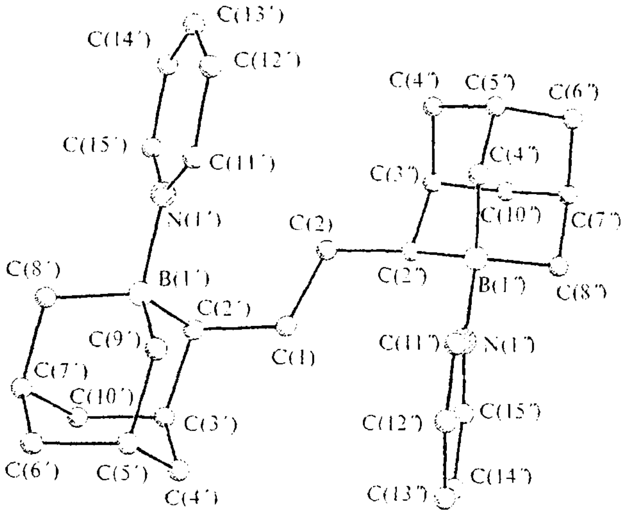


Fig. 1. Overall view of molecule 3.

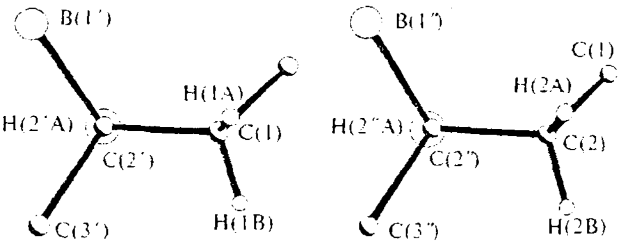


Fig. 2. Projections along the C(2′)—H(2′A) and C(2″)—H(2″A) bonds in molecule 3.

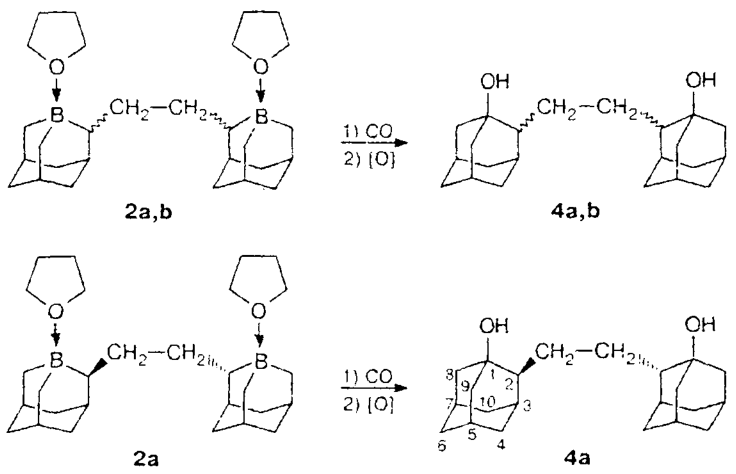
The geometric parameters of the 1-boraadamantyl fragments are somewhat asymmetrical, which is manifested in the following facts. First, two B—C bonds are somewhat shorter than the third bond (the B(1′)—C(2′) bond length is 1.636(8) Å and the average length of the remaining two bonds is 1.594 Å; the B(1″)—C(2″) bond length is 1.629(9) Å and the average length of the remaining two bonds is 1.618 Å). Second, the C—C bonds between the atoms of the BC(2)C(8)C(9) fragment and the six-membered chair-like C(3)C(4)C(5)C(6)C(7)C(10) ring are longer than the bonds in the latter ring. Thus the C(2)—C(3), C(8)—C(7), and C(9)—C(5) bond lengths are in the range of 1.523—1.560 Å and the C—C bond lengths in the rings are in the range of 1.503—1.540 Å. Finally, the BCC bond angles are somewhat smaller than the CCC bond angles (the average values are 106.80 and 110.16°, respectively). An analogous asymmetry was also observed in the three previously studied 1-boraadamantane complexes with pyridine,[6] quinoline,[6] and methylenetriphenylphosphorane,[7] in which the B substituents are located asymmetrically with respect to the 1-boraadamantanyl fragments, as in compound 3. The B—C bond lengths are 1.616 and 1.620 Å in the pyridine complex,[6] 1.60(1), 1.597(9), and 1.64(1) Å in the quinoline complex,[6] and 1.619, 1.630, and 1.634 Å in the methylenetriphenylphosphorane complex,[7] whereas the C—C bond lengths in these complexes are in the ranges of 1.522—1.547, 1.505—1.557, and 1.497—1.546 Å, respectively. In the 1-boraadamantane complex with 3,5-dimethyl-1-azaadamantane,[8] in which the 1-azaadamantane ligand is located symmetrically with respect to the 1-boraadamantane fragment, the B—C bond lengths are equalized (1.625—1.628 Å) and the C—C bond lengths vary in the range of 1.528—1.545 Å. In this case, an elongation of the C—C bonds between the BC_3 fragment and the six-membered ring is retained (and is even more pronounced; 1.539—1.545 Å). Therefore, it is believed that the steric factors that appear in the case of intermolecular contacts between the atoms of the 1-boraadamantane fragments and the B substituents affect primarily the B—C bond lengths and the BCC bond angles, whereas the asymmetry of the C—C bonds is, apparently, an inherent characteristic feature of the boraadamantane molecule.

The dative B→N bond length (1.641 Å) in compound 3 coincides with that observed[6] in the 1-boraadamantane complex with Py (1.642(4) Å), but it is shorter than those in the complexes with quinoline[6] (1.722(7) Å) and 1-azaadamantane[8] (1.690(3) Å). The B→N(Py) bond lengths (the B atom is bound to three carbon atoms) available in the Cambridge Structural Database (April 1999) differ substantially: 1.657,[9] 1.680,[10] 1.641,[11] 1.610,[12] and 1.630 Å.[13]

No pronounced dependence of the B→N bond length on the nature of the substituents in the B- and N-containing fragments of the molecules is observed. It can be suggested that the B→N bond length is not a fixed value and is determined both by the electronic (the character of the bonds with the boron and nitrogen atoms) and steric factors, which hinder the approach of the B-containing fragments to the N-containing fragments. Examination of all B→N bonds in the molecules with different types of the bonds with the participation of the boron atoms, *viz.*, the $C_3B{\to}N$, $C_2NB{\to}N$, and $C_2OB{\to}N$ bonds, demonstrated that the average values of the B→N bond lengths are 1.626 (1.539—1.783), 1.591 (1.522—1.701), and 1.631 Å (1.530—1.719), respectively. Such substantial spread in the bond lengths and the large mean error (0.2 Å) also agree with the suggestion that the B→N bonds are nonrigid.

One of the efficient ways of using boron cage compounds in organic synthesis involves their transformations into the corresponding adamantanols by carbonylation-oxidation reactions (direct replacement of the boron atoms by the carbon atoms).[1,14] The diastereomeric tetrahydrofuran complexes of 1,2-bis(1-boraadamantan-2-yl)ethane (**2a**, **2b**) which were synthesized in this work were smoothly converted into the corresponding 1,2-bis(1-hydroxyadamantan-2-yl)ethane (**4**). In this case, we obtained both a mixture of diastereomeric diadamantanols (**4a,b**) and an individual racemate (**4a**) (Scheme 2).

Scheme 2



To summarize, in this work we synthesized the first representatives (complexes) of bis-1-boraadamantane compounds and carried out their conversions into diastereomeric 1,2-bis(1-hydroxyadamantan-2-yl)ethanes.

Experimental

All operations with organoboron compounds were carried out under an atmosphere of dry argon. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on Bruker AC-200P (operating at 200.13, 50.32, and 64.21 MHz for ^{1}H, ^{13}C, and ^{11}B, respectively) and Bruker AMX-400 (operating at 400.13 and 100.13 MHz for ^{1}H and ^{13}C, respectively) instruments.

1,4-Bis(3-methoxy-3-borabicyclo[3.3.1]non-6-en-7-yl)butane (1). Octa-1,7-diyne (14.6 g, 135 mmol) was added dropwise to triallylborane (36.8 g, 270 mmol) at 135—140 °C for 1 h. The reaction mixture was heated at 140 °C for 2 h and then cooled to 0 °C. MeOH (15 mL) was carefully added and the reaction mixture was refluxed for 1 h. Distillation gave compound **1** in a yield of 36.8 g (75%), b.p. 179—182 °C (0.2 Torr); n_D^{20} 1.5168. Found (%): C, 74.80; H, 10.49; B, 6.00. $C_{22}H_{36}B_2O_2$. Calculated (%): C, 74.61; H, 10.25; B 6.10. ^{1}H NMR (CDCl$_3$), δ: 0.78—2.50 (m, 28 H, signals for the aliphatic protons); 3.61 (s, 6 H, OMe); 5.39 (m, 2 H, HC=C). ^{13}C NMR (CDCl$_3$), δ: 24.3 and 25.5 (C(2) and C(4)); 27.18 and 27.23 (CH$_2$ bridge); 27.5 and 29.2 (C(1) and C(5)); 32.7 and 37.3 (C(8) and C(9)); 37.48 and 37.51 ($\underline{C}H_2$—C=C); 52.9 (MeO); 127.9 ($\underline{C}$H=C); 134.0 (CH=$\underline{C}$).

Complexes of (*RS,RS*)- (2a) and (*RS,SR*)-1,2-bis(1-boraadamantan-2-yl)ethane (2b) with THF. A 1.2 *M* solution of BH$_3$ in THF (50 mL) was added dropwise to a solution of compound **1** (10 g, 28.3 mmol) in THF (150 mL). The reaction mixture was refluxed for 2 h and then cooled. The THF (~50 mL) was evaporated *in vacuo*. After 16 h, the crystals that precipitated were filtered off. According to the ^{13}C NMR spectral data (Table 1), the resulting compound was pure racemate **2a**. The yield was 2.98 g (24% or 48% per diastereomer), m.p. 188—189 °C. ^{11}B NMR (CDCl$_3$), δ: 11.8. ^{1}H NMR (THF-d$_8$), δ: 0.40—2.20 (m, 40 H, protons of the adamantane core and CH$_2$ groups); 3.69 (m, 8 H, CH$_2$OCH$_2$ in THF). The ^{13}C NMR spectrum is given in Table 1. The mother liquor was concentrated *in vacuo*, and complex **2** was additionally obtained in a yield of 8.68 g (70%), which was (according to the ^{13}C NMR spectral data) a 2 : 1 mixture of *meso* form **2b** and racemate **2a**. The total yield of compounds **2a** and **2b** was 94%.

Complex of (*RS,RS*)-1,2-bis(1-boraadamantan-2-yl)ethane with pyridine (3). Pyridine (0.3 mL, 3.7 mmol) was added to a solution of compound **2a** (0.5 g, 1.1 mmol) in THF (50 mL). The solvent was removed *in vacuo*. The residue was twice recrystallized from EtOH. Complex **3** was obtained in a yield of 0.4 g (72%), m.p. 214—215 °C. Found (%): C, 79.59; H, 10.08; B, 4.28. $C_{30}H_{42}B_2N_2$. Calculated (%): C, 79.67; H, 9.36; B, 4.78. ^{1}H NMR (Py-d$_5$), δ: 0.50—2.60 (m, 32 H, protons of the adamantane core and CH$_2$ groups); 7.28 (dd, 4 H, *m*-Py, J = 7.6 Hz and J = 3.8 Hz); 7.65 (t, 2 H, *p*-Py, J = 7.6 Hz); 8.78 (d, 4 H, *o*-Py). The ^{13}C NMR spectrum is given in Table 1.

(*RS,RS*)-1,2-Bis(1-hydroxyadamantan-2-yl)ethane (4a). A solution of compound **2a** (3.25 g, 7.4 mmol) in THF (90 mL) was heated in an autoclave filled with CO (the initial pressure was 100 atm) at 140 °C for 3 h. The autoclave was cooled and ethylene glycol (2.5 mL) was added to the reaction mixture. Then the mixture was heated at 140 °C and at a CO pressure of 70 atm for 4 h. After cooling, the content of the autoclave was transferred into a flask. A mixture of EtOH (15 mL) and a 10% NaOH solution (10 mL) was added to the reaction mixture at 0 °C and then a 45% H$_2$O$_2$ solution (1 mL, 16 mmol) was carefully added. The reaction mixture was kept at ~20 °C for 16 h and then refluxed for 15 h. The THF was removed *in vacuo*, and the residue was filtered off and washed with water and ether. The residue was recrystallized from *n*-BuOH. Product **4a** was obtained in a yield of 1.4 g (63%), m.p. 307—308 °C. Found (%): C, 79.65; H, 10.37. $C_{22}H_{34}O_2$. Calculated (%): C, 79.95; H, 10.37. ^{1}H NMR (DMSO-d$_6$), δ: 1.25—2.10 (m, 32 H, protons of the adamantane core and CH$_2$ groups); 3.34 (s, 2 H, OH). ^{13}C NMR (DMSO-d$_6$), δ: 23.5 (CH$_2$ bridge); 29.8 (C(4)); 29.6, 30.3, and 31.1 (C(3), C(5), and C(7)); 36.8, 37.9, and 39.2 (C(6), C(9), and C(10)); 47.4 (C(8)); 50.3 (C(2)); 67.8 (C(1)).

1,2-Bis(1-hydroxyadamantan-2-yl)ethane (a mixture of the *meso* form and the racemate, 1 : 1 (4a,b)). A mixture of alcohols **4a,b** was prepared from a mixture of complexes **2a,b** (9 g, 20 mmol) taken in a ratio of 1 : 1 in a yield of 4.7 g (76%) as described above; m.p. 300—306 °C. Found (%): C, 79.45;

Table 2. Selected bond lengths (*d*) in molecule **3**

Bond	*d*/Å	Bond	*d*/Å
B(1′)—C(9′)	1.583(8)	B(1″)—C(8″)	1.616(8)
B(1′)—C(8′)	1.606(8)	B(1″)—C(9″)	1.620(8)
B(1′)—C(2′)	1.636(9)	B(1″)—C(2″)	1.629(9)
B(1′)—N(1′)	1.652(7)	B(1″)—N(1″)	1.630(8)
C(2′)—C(3′)	1.560(8)	C(2″)—C(3″)	1.533(8)
C(3′)—C(4′)	1.510(9)	C(3″)—C(10″)	1.516(8)
C(3′)—C(10′)	1.540(8)	C(3″)—C(4″)	1.548(9)
C(10′)—C(7′)	1.520(9)	C(10″)—C(7″)	1.516(9)
C(7′)—C(6′)	1.511(8)	C(7″)—C(6″)	1.523(9)
C(7′)—C(8′)	1.535(8)	C(7″)—C(8″)	1.514(8)
C(6′)—C(5′)	1.529(8)	C(6″)—C(5″)	1.524(9)
C(5′)—C(4′)	1.503(9)	C(5″)—C(4″)	1.510(9)
C(5′)—C(9′)	1.556(8)	C(5″)—C(9″)	1.532(8)

H, 13.23. $C_{22}H_{34}O_2$. Calculated (%): C, 79.95; H, 10.37. ^1H NMR (DMSO-d_6), δ: 1.00—2.10 (m, 32 H, protons of the adamantane core and CH_2 groups); 3.38 (s, 2 H, OH). ^{13}C NMR (DMSO-d_6), δ: 23.5 and 24.7 (CH_2 bridge); 29.8 and 30.0 (C(4)); 29.6, 30.3, 31.1, and 31.7 (C(3), C(5), and C(7)); 36.8, 37.9, and 39.2 (C(6), C(9), and C(10)); 47.4 (C(8)); 50.3 and 51.0 (C(2)); 67.8 and 67.9 (C(1)).

X-ray diffraction analysis of compound 3. Colorless crystals of **3** prepared by recrystallization from 96% EtOH, $C_{30}H_{42}B_2N_2$ (M = 452.28), are triclinic, at 20 °C a = 10.530(3) Å, b = 10.869(3) Å, c = 12.247(4) Å, α = 74.64(2)°, β = 71.35(2)°, γ = 83.31(3)°, V = 1279.9(7) Å^3, space group $P\bar{1}$, d_{calc} = 1.174 g cm^{-3} for Z = 2. The intensities of 3898 reflections were collected on an automated Enraf-Nonius CAD-4 diffractometer (Mo-Kα radiation, graphite monochromator, θ/5/3θ scanning technique) at –20 °C in the region of up to θ_{max} = 23°. After averaging of equivalent reflections, 3549 independent reflections were obtained. These reflections were used in the structure solution. The positions of all nonhydrogen atoms were determined by direct methods and refined by the least-squares method based on F^2_{hkl}. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. The final R factors were as follows: R_1 = 0.0746 (calculated using F_{hkl} for 1366 reflections with $I > 2\sigma(I)$), wR_2 = 0.2519 (calculated using F^2_{hkl} for all 3488 reflections used in the refinement of 307 independent parameters). All calculations were performed using the SHELXTL PLUS 5 program package.[15]

Selected bond lengths are given in Table 2.

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