REACTION OF 1,2-BORYLPHOSPHINOETHENE WITH THIOCYANATES. MOLECULAR AND CRYSTAL STRUCTURE OF 2,2,3-TRIBUTYL-4,5,5-TRIPHENYL-6-METHYLTHIO-1,5,2-AZAPHOSPHONIABORATACYCLOHEXA-3,6-DIENE

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The reaction of 1,2-borylphosphinoethenes with alkylthiocyanates leads to formation of substances having the structure of 6-alkylthio-1,5,2-azaphosphoniaboratacyclohexa-3,6-dienes in the crystal state. The structure of the compounds has been proven by x-ray diffraction analysis of 2,2,3-tributyl-4,4,5-triphenyl-5-methylthio-1,5,2-azaphosphoniaboratacyclohexa-3,6-diene. The heterocyclic moiety of the molecule is planar within 0.010(2) Å. The methylthio group lies practically in the plane of the heterocycle.

Keywords: *1,2-borylphosphinoethene, alkylthiocyanate, 6-alkylthio-1,5,2-azaphosphoniaboratacyclohexa-3,6-diene, structure.*

We know [1, 2] that alkylthiocyanates react with esters of P(III) acids, trimethylsilyl- and tetraalkylpyrophosphites according to the Arbuzov reaction scheme with formation of thiolphosphates and the corresponding cyanides. In these reactions, the cyano group in the alkylthiocyanates behaves like a pseudohalogen. At the same time, when alkylthiocyanates react with aminophosphines, the multiple-bond properties of the cyano group are also displayed along with pseudohalogen properties. In addition to the corresponding aminophosphine sulfides, the reaction products include polycyanated phosphazo compounds [3], the formation of which is due to occurrence of homolytic processes, in particular addition of radical particles at the $C\equiv N$ bond of the thiocyanates. Highly nucleophilic dithio- and monothiophosphoric acids can be added at the $C\equiv N$ bond of the thiocyanates [4, 5]. In this case, the cyano group displays the properties of an electrophilic multiple bond. In this case, an important role is played by protonation of the nitrogen atom (protophilic assistance to nucleophilic addition). In reactions of salts of thiophosphoric acids with thiocyanates, where such assistance is excluded, full thiophosphates and salts of thiocyanic acid are formed, i.e., the pseudohalogen properties are displayed even by the thiocyanate group as a whole.

The presence in the 1,2-borylphosphinoethene molecule (**1**) of both nucleophilic (P(III)) and electrophilic (B(III)) reaction centers allowed us to assume that they would be capable of entering into the cycloaddition reaction at the polarized $C\equiv N$ bond of the thiocyanates. For **1**, such reactions are characteristic. In particular, in reactions with aldehydes, 1,2-borylphosphinoethenes form cyclic betaines. Reaction with CS_2 occurs analogously to the [4 + 2]-cycloaddition type. The reaction of **1** with azacumulenes (isocyanates, isothiocyanates, carbodiimides [7, 8]) is accomplished as [4 + 2]-cycloaddition at the $C\equiv N$ moiety and does not involves the C=O and C=S bonds. Furthermore, the betaines formed can be isomerized to bicyclic compounds (in some cases reversibly) [8]. The isomerization process is involved in migration of the Bu anion between the *sp*^{3} C and B atoms.

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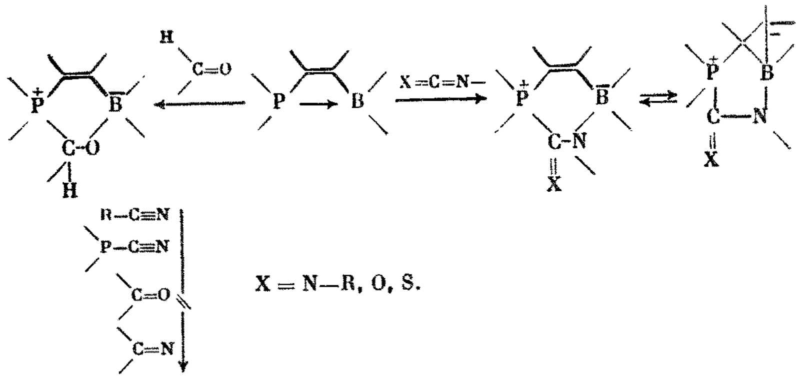
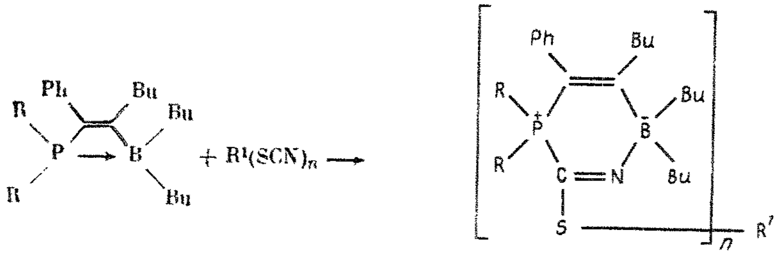


X = N—R, O, S.

Moreover, 1,2-borylphosphinoethenes do not react with ketones, azomethines, nitriles, trimethylsilylcyanide, or cyanophosphines. Therefore we cannot *a priori* exclude the possibility of reaction of thiocyanates with **1** by breaking of the S−C bond, analogously to their reactions with P(III) derivatives.

The reaction of 1,2-borylphosphinoethene with alkylthiocyanates was accomplished in C_6H_6 or in the absence of solvent at ~20°C. The reactions are accompanied by a moderate amount of evolution of heat, and after 5 h crystallization occurs of 6-alkylthio-1,5,2-azaphosphoniaboratacyclohexa-3,6-dienes **1-4**:



(1) - (4)

R=Et, R'=Me, n=1 (**1**); R=Ph, R'=Me, n=1 (**2**);
R=Ph, R'=Bn, n=1 (**3**); R=Ph, R'=—CH_2—, n=2 (**4**).

In the IR spectra of the crystalline substances **1-4**, the absorption band characteristic for the C≡N group is missing and absorption bands are present which can be assigned to the C=N group (1620 cm^{-1}) and the C=C bond (1550 cm^{-1}). In the PMR spectra of solutions of **1-4**, the ratio of the integrated intensities of the proton groups corresponds to the presence of all the functional groups present in the starting reagents. Note the magnitude of the chemical shifts in the ^{31}P NMR spectra of compounds **1-4**, in which we observe one signal for each with chemical shifts equal to −22 ppm for (**1**) and −37-38 ppm for **2-4**.

The structure of the compounds in the crystalline state was confirmed by x-ray diffraction analysis of substance **2**. The coordinates of the nonhydrogen atoms are presented in Table 1. The molecular geometry is shown in Fig. 1. The bond lengths, the bond angles, and the torsional angles are presented in Tables 2-4 respectively.

The heterocycle of molecule **2** is planar within 0.010(2) Å; the S^1 and C^{34} atoms lie practically in this plane (the deviations of these atoms are 0.097(1) and 0.056(2) Å. The key atom of the Ph substituent at the $C^5(C^{28})$ atom deviates from this plane by 0.204(2) Å. The methylthio group at the C^3 atom also lies practically in the plane of the heterocycle: the dihedral angle between these planes is 10.3(2)°. The planes of the zigzag butyl substituents at the B^1 and C^6 atoms are almost perpendicular to the plane of the heterocycle (the dihedral angles between the planes of the substituents are 86.1(1), 81.4(1), and 80.0(1)° respectively). The planes of the Ph substituents at the P atom are also almost orthogonal to the plane of the heterocycle: the dihedral angles between them are 80,4(1) and 105.4(1)° respectively.

A planar conformation of the cyclophosphahexadiene ring, similar to that found in molecule **2**, is observed in the molecule of the dibromide of 1,1,4,4-tetraethyl-2,5-dimethyl-1,4-diphosphonium cyclohexa-2,5-diene [9]. In molecule **2**, the lengths of the endocyclic P−C bonds are markedly different and are equal to 1.832(2) Å (P^4-C^3) and 1.774(2) Å (P^4-C^5); the lengths of the double bonds are 1.239(2) Å (C^3=N^2) and 1.347(3) Å (C^5=C^6). In the molecule of the dibromide of 1,1,4,4-tetraethyl-2,5-dimethyl-1,4-diphosphonium cyclohexa-1,5-diene [9], the length of the endocyclic P−C bonds was 1.788 Å, the length of the

TABLE 1. Coordinates of Atoms and Their Equivalent Isotropic Temperature Factors

$$B_{\text{iso}}^{\text{eq}} = {}^4/_3 \sum_{i=1}^{3}\sum_{j=1}^{3} B(i,j)(\vec{a}_i, \vec{a}_j)$$

Atom	X	Y	Z	B
S^1	−0.02118(5)	0.21905(5)	−0.30982(4)	4.06(1)
P^4	0.14735(5)	0.38808(4)	−0.27846(3)	2.75(1)
N^2	0.2583(2)	0.1204(1)	−0.26230(9)	2.98(3)
C^3	0.1516(2)	0.2193(2)	−0.2814(1)	2.82(4)
C^5	0.3178(2)	0.7365(2)	−0.2452(1)	2.77(4)
C^6	0.4186(2)	0.2574(2)	−0.2263(1)	2.79(4)
C^7	0.5527(2)	0.0173(2)	−0.2979(1)	3.77(5)
C^8	0.5794(3)	0.0763(3)	−0.3758(2)	5.48(7)
C^9	0.7063(4)	−0.0198(3)	−0.04366(2)	8.57(9)
C^{10}	0.7274(6)	0.0450(5)	−0.5140(3)	15.8(2)
C^{11}	0.4054(2)	0.0444(2)	−0.1480(1)	3.62(5)
C^{12}	0.2642(3)	0.1136(2)	−0.0859(1)	4.32(5)
C^{13}	0.2649(3)	0.0475(3)	−0.0088(2)	6.71(8)
C^{14}	0.1169(4)	0.1060(3)	−0.0495(2)	7.42(9)
C^{15}	0.0014(2)	0.0526(2)	−0.2879(2)	5.14(6)
C^{16}	−0.0230(2)	0.4945(2)	−0.2134(1)	3.25(4)
C^{17}	−0.0223(2)	0.4864(2)	−0.1331(1)	3.97(5)
C^{18}	−0.1514(3)	0.5632(3)	−0.0803(2)	5.26(6)
C^{19}	−0.2810(3)	0.6489(3)	−0.1080(2)	6.25(7)
C^{20}	−0.2844(3)	0.6541(3)	−0.1855(2)	6.91(8)
C^{21}	−0.1561(3)	0.5782(3)	−0.2396(2)	5.29(7)
C^{22}	−0.1445(2)	0.4539(2)	−0.3749(1)	3.58(4)
C^{23}	0.1075(3)	0.5888(2)	−0.3854(2)	4.96(6)
C^{24}	0,1262(3)	0.6321(3)	−0.4610(2)	6.46(7)
C^{25}	0.1808(3)	0.5425(3)	−0.5250(2)	6.26(7)
C^{26}	0.2161(3)	0.4098(3)	−0.5147(2)	5.47(7)
C^{27}	0.1985(2)	0.3653(2)	−0.4400(1)	4.11(5)
C^{28}	0.3375(2)	0.5067(2)	−0.2513(1)	3.15(4)
C^{29}	0.4235(2)	0.5291(2)	−0.3179(2)	4.49(5)
C^{30}	0.4202(3)	0.6537(2)	−0.3277(2)	5.76(6)
C^{31}	0.3523(3)	0.7547(2)	−0.2711(2)	5.32(6)
C^{32}	0.2702(3)	0.7327(2)	−0.2049(2)	4.82(6)
C^{33}	0.2615(2)	0.6097(2)	−0.1943(1)	3.82(5)
C^{34}	0.5646(2)	0.2549(2)	−0.2014(1)	3.38(4)
C^{35}	0.5465(2)	0.2996(2)	−0.1158(1)	4.04(5)
C^{36}	0.6981(3)	0.3279(3)	−0.0951(2)	5.10(6)
C^{37}	0.6893(3)	0.3279(3)	−0.0107(2)	6.16(7)
B^1	0.4062(2)	0.1138(2)	−0.2330(1)	3.09(5)

C═C bonds was 1.340 Å. In this molecule and in compound **2**, the endocyclic P−C and C═C bonds have the typical length, which suggests the absence of delocalization of electron density in these planar rings. We should note that in the structure of the dibromide of 1,1,2,4,4,5-hexaphenyl-1,4-diphosphonium cyclohexa-2,5-diene [10], the heterocycle has the boat conformation; in this case, the P−C bond lengths (1.80 Å) and the C═C bond lengths (1.33 Å) in it, within experimental error limits, are close to those found in molecule **2**. The endocyclic $C^3P^4C^5$ bond angle in molecule **2** is equal to 107.30(9)°, which is close to the values determined in the reference molecules (110.1(3) [9] and 107° [10]). As a characteristic feature of molecule **2** we should include the appreciable lengthening of the endocyclic P^4-C^3 bond (1.832(2) Å), which is probably due to the effect of the thio group. The B−C bond lengths are the same within experimental error limits (1.637(4) Å avg.). The N−B bond length is equal to 1.555(3) Å.

Thus we have shown that upon reaction of 1,2-borylphosphinoethenes with alkylthiocyanates, substances are formed which in the crystalline state have the structure of 6-alkylthio-1,5,2-azaphosphoniaboratacyclohexa-3,6-dienes.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on the Bruker WM-250 spectrometer. The PMR spectra were obtained on the Varian T-60 spectrometer at 34.5°C, external standard TMS. The IR spectra were recorded in a vaseline suspension on the UR-20 spectrometer.

2,2,3-Tributyl-4-phenyl-5,5-diethyl-6-methylthio-1-aza-5-phosphonia-2-boratacyclohexa-3,6-diene (1). 0.08 g (1 mmoles) methylthiocyanate was added to 0.4 g (1 mmoles) 1,1,2-tributyl-3-phenyl-4,4-diethyl-4-phosphonia-1-boratacyclobut-2-

TABLE 2. Bond Lengths d (Å)

Bond	d	Bond	d
S^1-C^3	1.802(2)	$C^{16}-C^{21}$	1.380(4)
S^1-C^{15}	1.786(3)	$C^{17}-C^{18}$	1.379(3)
P^4-C^3	1.832(2)	$C^{18}-C^{19}$	1.376(4)
P^4-C^5	1.774(2)	$C^{19}-C^{20}$	1.342(5)
P^4-C^{16}	1.796(3)	$C^{20}-C^{21}$	1.385(4)
P^4-C^{22}	1.800(3)	$C^{22}-C^{23}$	1.388(3)
N^2-C^3	1.239(2)	$C^{23}-C^{24}$	1.388(4)
N^2-B^1	1.555(3)	$C^{24}-C^{25}$	1.380(5)
C^5-C^6	1.347(3)	$C^{25}-C^{26}$	1.367(5)
C^5-C^{28}	1.509(2)	$C^{26}-C^{27}$	1.377(3)
C^6-C^{34}	1.518(3)	$C^{28}-C^{33}$	1.388(3)
C^7-C^8	1.508(4)	$C^{29}-C^{30}$	1.396(3)
C^7-B^1	1.643(4)	$C^{30}-C^{31}$	1.372(4)
C^8-C^9	1.517(5)	$C^{31}-C^{32}$	1.352(4)
C^9-C^{10}	1.522(9)	$C^{32}-C^{33}$	1.388(4)
$C^{11}-C^{12}$	1.515(3)	$C^{34}-C^{35}$	1.527(3)
$C^{12}-C^{13}$	1.501(4)	$C^{36}-C^{37}$	1.506(5)
$C^{13}-C^{14}$	1.508(5)		
$C^{16}-C^{17}$	1.389(4)		

TABLE 3. Bond Angles ω (deg)

Angle	ω	Angle	ω
$C^3S^1C^{15}$	100.1(1)	$C^{18}C^{19}C^{20}$	120.5(3)
$C^3P^4C^5$	107.30(9)	$C^{19}C^{20}C^{21}$	121.1(3)
$C^3P^4C^{16}$	109.08(9)	$C^{16}C^{21}C^{20}$	119.5(3)
$C^3P^4C^{22}$	110.61(9)	$P^4C^{22}C^{23}$	121.2(2)
$C^5P^4C^{16}$	111.58(9)	$P^4C^{22}C^{27}$	118.7(2)
$C^5P^4C^{22}$	109.19(9)	$C^{22}C^{23}C^{27}$	119.7(3)
$C^{16}P^4C^{22}$	109.1(1)	$C^{22}C^{23}C^{24}$	119.1(3)
$C^3N^2B^1$	128.5(2)	$C^{23}C^{24}C^{25}$	120.5(3)
$S^1C^3P^4$	111.5(1)	$C^{24}C^{25}C^{26}$	120.4(3)
$S^1C^3N^2$	125.4(1)	$C^{25}C^{26}C^{27}$	119.9(4)
$P^4C^3N^2$	122.9(1)	$C^{22}C^{27}C^{26}$	121.8(2)
$P^4C^5C^6$	119.9(1)	$C^5C^{28}C^{29}$	119.6(2)
$P^4C^5C^{28}$	111.8(1)	$C^5C^{28}C^{33}$	121.8(2)
$C^6C^5C^{28}$	128.0(2)	$C^{29}C^{28}C^{33}$	118.4(2)
$C^5C^6C^{34}$	116.7(2)	$C^{28}C^{29}C^{30}$	120.3(3)
$C^5C^6B^1$	126.9(2)	$C^{29}C^{30}C^{31}$	120.4(3)
$C^{34}C^6B^1$	116.3(2)	$C^{30}C^{31}C^{32}$	119.8(2)
$C^8C^7B^1$	116.3(2)	$C^{31}C^{32}C^{33}$	120.6(3)
$C^7C^8C^9$	114.8(3)	$C^{28}C^{33}C^{32}$	120.6(2)
$C^8C^9C^{10}$	112.4(5)	$C^6C^{34}C^{35}$	115.0(2)
$C^{12}C^{11}B^1$	116.2(2)	$C^{34}C^{35}C^{36}$	111.6(3)
$C^{11}C^{12}C^{13}$	115.4(2)	$C^{35}C^{36}C^{37}$	114.3(3)
$C^{12}C^{13}C^{14}$	115.6(3)	$N^2B^1C^6$	114.6(2)
$P^4C^{16}C^{17}$	118.0(2)	$N^2B^1C^7$	106.1(2)
$P^4C^{16}C^{21}$	123.0(2)	$N^2B^1C^{11}$	105.5(2)
$C^{17}C^{16}C^{21}$	118.9(3)	$C^6B^1C^7$	108.0(2)
$C^{16}C^{17}C^{18}$	120.5(2)	$C^6B^1C^{11}$	111.8(2)
$C^{17}C^{18}C^{19}$	119.4(3)	$C^7B^1C^{11}$	110.8(2)

TABLE 4. Torsional Angles τ (deg)

Angle	τ	Angle	τ
$N^2C^3P^4C^5$	0.3(2)	$C^{15}S^1C^3N^2$	−7.8(2)
$C^3P^4C^5C^6$	−1.3(2)	$C^3P^4C^{16}C^{17}$	78.3(2)
$P^4C^5C^6B^1$	2.2(3)	$C^5P^4C^{16}C^{17}$	−40.1(2)
$C^5C^6B^1N^2$	−1.8(3)	$C^3P^4C^{22}C^{23}$	165.7(2)
$C^6B^1N^2C^3$	0.7(3)	$C^3P^4C^{22}C^{27}$	−22.1(2)
$B^1N^2C^3P^4$	−0.1(3)	$C^5P^4C^{22}C^{23}$	−76.4(2)
$C^{15}S^1C^3P^4$	−166.9(1)		

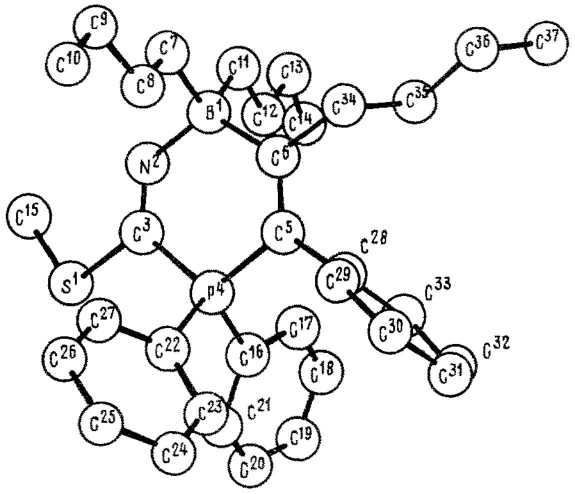


Fig. 1. Molecular structure of 2,2,3-tributyl-4,5,5-triphenyl-6-methylthio-1,5,2-azaphosphoniaboratacyclohexa-3,6-diene.

ene. At the end of the exothermic reaction, the precipitated crystals were filtered off and washed with acetonitrile. Yield of **1**, 0.21 g (44%). An analytically pure sample was obtained by recrystallization from acetonitrile, mp 81-83°C. Found: C 70.61, H 10.24, N 3.30, P 6.91, S 7.80%. $C_{26}H_{45}BNPS$. Calculated: C 70.11, H 10.11, N 3.15, P 6.96, S 7.19%. IR spectrum (ν, cm^{-1}): 1625 (C=N). ^1H NMR spectrum (d_6-acetone, δ, ppm): 0.27-2.50 m (37H, $C_4H_9+C_2H_5$), 2.63 s (3H, SMe), 6.90-7.43 m (5H, H_{arom}). ^{31}P NMR spectrum (C_6H_6, δ, ppm): -22.

2,2,3-Tributyl-4,5,5-triphenyl-6-methylthio-1-aza-5-phosphonia-2-boratacyclohexa-3,6-diene(2).0.15g(2mmoles) methylthiocyanate was added to 0.98 g (2 mmoles) of the corresponding 1,2-borylphosphinoethene in 3 ml dry C_6H_6. After 4 h, the solvent was removed under vacuum, the residue was crystallized from acetonitrile. Yield of **2**, 0.76 g (67%), mp 61-63°C. Found: C 75.97, H 8.43, N 2.55, P 6.12, S 6.02%. $C_{34}H_{45}BNPS$. Calculated: C 74.41, H 8.32, N 2.59, P 5.73, S 5.91%. IR spectrum (ν, cm^{-1}): 1620 (C=N). ^1H NMR spectrum (d_6-acetone, δ, ppm): 0.47-1.87 m (27H, C_4H_9), 2.7 s (3H, SMe), 6.50-7.93 m (15H, H_{arom}). ^{31}P NMR spectrum (C_6H_6, δ, ppm): -38.

2,2,3-Tributyl-4,5,5-triphenyl-6-benzylthio-1-aza-5-phosphonia-2-boratacyclohexa-3,6-diene (3). Obtained analogously to **2**. Yield 65%, mp 67-68°C. Found: C 78.05, H 8.07, N 2.23, P 5.18, S 5.69%. $C_{40}H_{49}BNPS$. Calculated: C 77.79, H 7.94, N 2.27, P 5.02, S 5.18%. IR spectrum (ν, cm^{-1}): 1625 (C=N). ^1H NMR spectrum (d_6-acetone, δ, ppm): 0.43-1.83 m (27H, C_4H_9), 4.37 s (2H, SCH_2), 6.53-7.83 m (20H, H_{arom}). ^{31}P NMR spectrum (C_6H_6, δ, ppm): -37.

Bis-(2,2,3-tributyl-4,5,5-triphenyl-1-aza-5-phosphonia-2-boratacyclohexa-3,6-dienyl-6-thio)methane(4).Obtained analogously to **2**. Yield 74%, mp 93-95°C. Found: C 75.86, H 8,25, N 2.76, P 6.28, S 6.47%. $C_{67}H_{86}B_2N_2P_2S_2$. Calculated: C 75.42, H 8.06, N 2.63, P 5.81, S 6.00%. IR spectrum (ν, cm^{-1}): 1630 (C=N). ^1H NMR spectrum (d_6-acetone, δ, ppm): 0.43-1.60 m (54H, C_4H_9), 4.63 s (2H, SCH_2S), 6.53-7.83 m (30H, H_{arom}). ^{31}P NMR spectrum (C_6H_6, δ, ppm): -38.

Crystals of **2**, $C_{34}H_{45}NBS$, mp 61-63°C, triclinic. At 20°C, a = 10.939(3), b = 10.939(3), c = 17.258(6) Å, α = 88.78(2), β = 10.939(3), γ = 66.48(4), $Z = 2$, d_{calc} = 1.10 g/cm^3, space group $P1$. Cell parameters and intensities of 3679 independent reflections with $F^2 \geq 3\sigma$ were measured on the Enraf-Nonius CAD-4 automatic four-circle diffractometer with K geometry (λ MoKα, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 25°$). The structure was deciphered by the direct method using the MULTAN program and refined first in the isotropic approximation and then in the anisotropic approximation. All the hydrogen atoms were determined from difference series and refined isotropically in the final stage. The final values of the R factors were R = 0.034, R_w = 0.050 from 3662 reflections with $F^2 \geq 6\sigma$.

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