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Synthesis and Structure of Sb-Containing Compounds of Binuclear Phenols

V. V. Sharutin, A. P. Pakusina, O. K. Sharutina, O. V. Subacheva, B. V. Bukvetskii, D. Yu. Popov, and A. V. Gerasimenko

Blagoveshchensk Pedagogical State University, ul. Lenina 104, Blagoveshchensk, 675000 Russia
Institute of Chemistry, Far East Division, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

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Abstract—The toluene solvate of 1-(tetraphenylstiboxy)-3-oxybenzene (**I**) was synthesized by reacting pentaphenylantimony with resorcin (at a molar ratio of 1 : 1) in toluene at 20°C, and the 1 : 3 complex (**II**)of 1,4-bis(tetraphenylstiboxy)benzene with hydroquinone was synthesized by reacting pentaphenylantimony with hydroquinone (at a molar ratio of 1 : 2) under similar conditions. The structures of the compounds obtained were determined using X-ray diffraction analysis. The Sb atoms in **I** and **II** have a distorted trigonal-bipyramidal coordination to the axial phenolate groups.

The syntheses of organoantimony derivatives of binuclear phenols from triphenylstibine (Ph_3Sb) and substituted *o*-benzoquinones or from triphenylantimony dihalides and *o*-substituted phenols were described in [1, 2]. These compounds can be obtained from triphenylantimony dichloride (Ph_3SbCl_2) and sodium salt of cathechol derivatives [3]. A promising method of synthesis of triphenylantimony aroxides from Ph_3Sb, binuclear phenol, and *tert*-buthyl hydroperoxide via the reaction of oxidative addition was reported in [4].

In this work, the synthesis of antimony-containing derivatives of binuclear phenols, namely, resorcin and hydroquinone, and their molecular and crystal structures are described.

RESULTS AND DISCUSSION

It was established that reaction of pentaphenylantimony with resorcin and hydroquinone in toluene is accompanied by the replacement of one or two hydro-

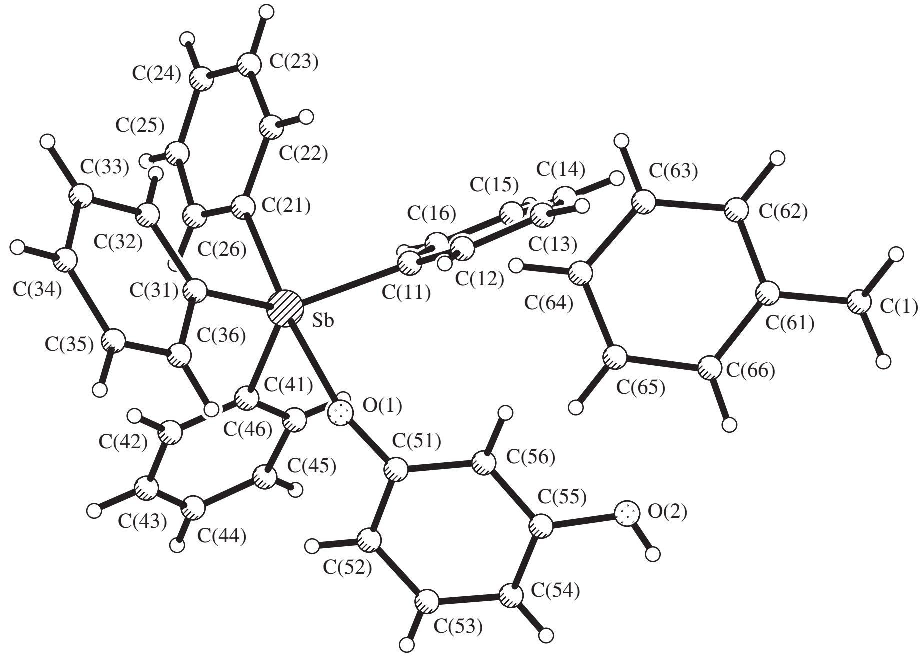

Fig. 1. Structure of complex **I**.

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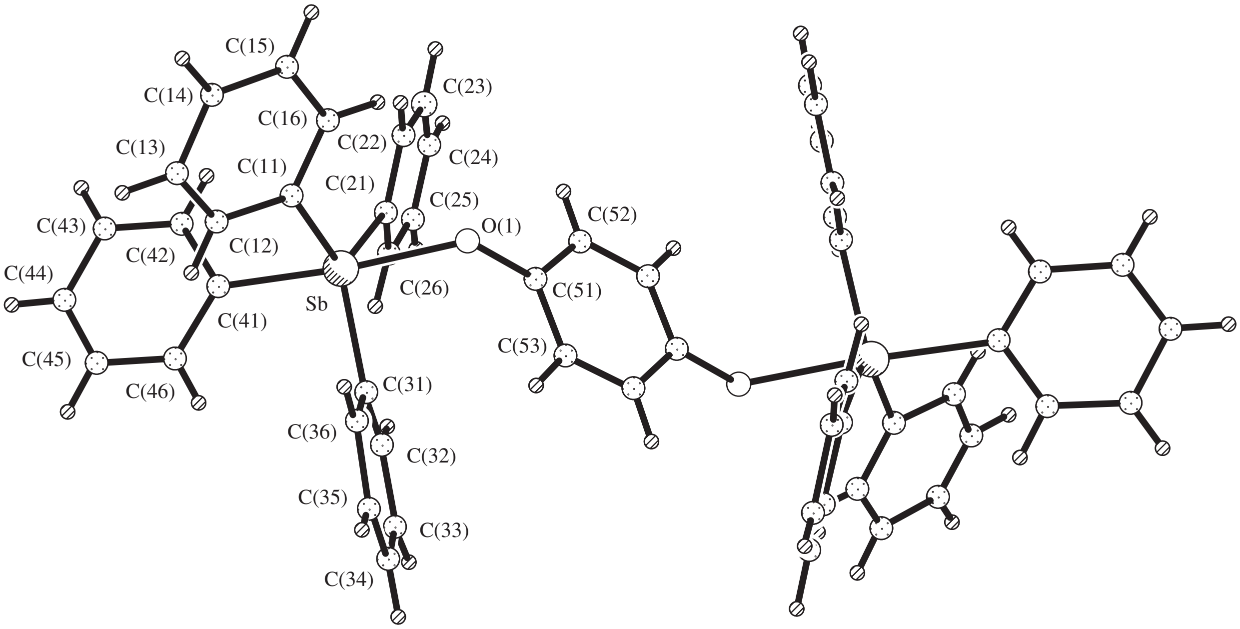

Fig. 2. Structure of 1,4-$(Ph_4SbO)_2C_6H_4$ in **II**.

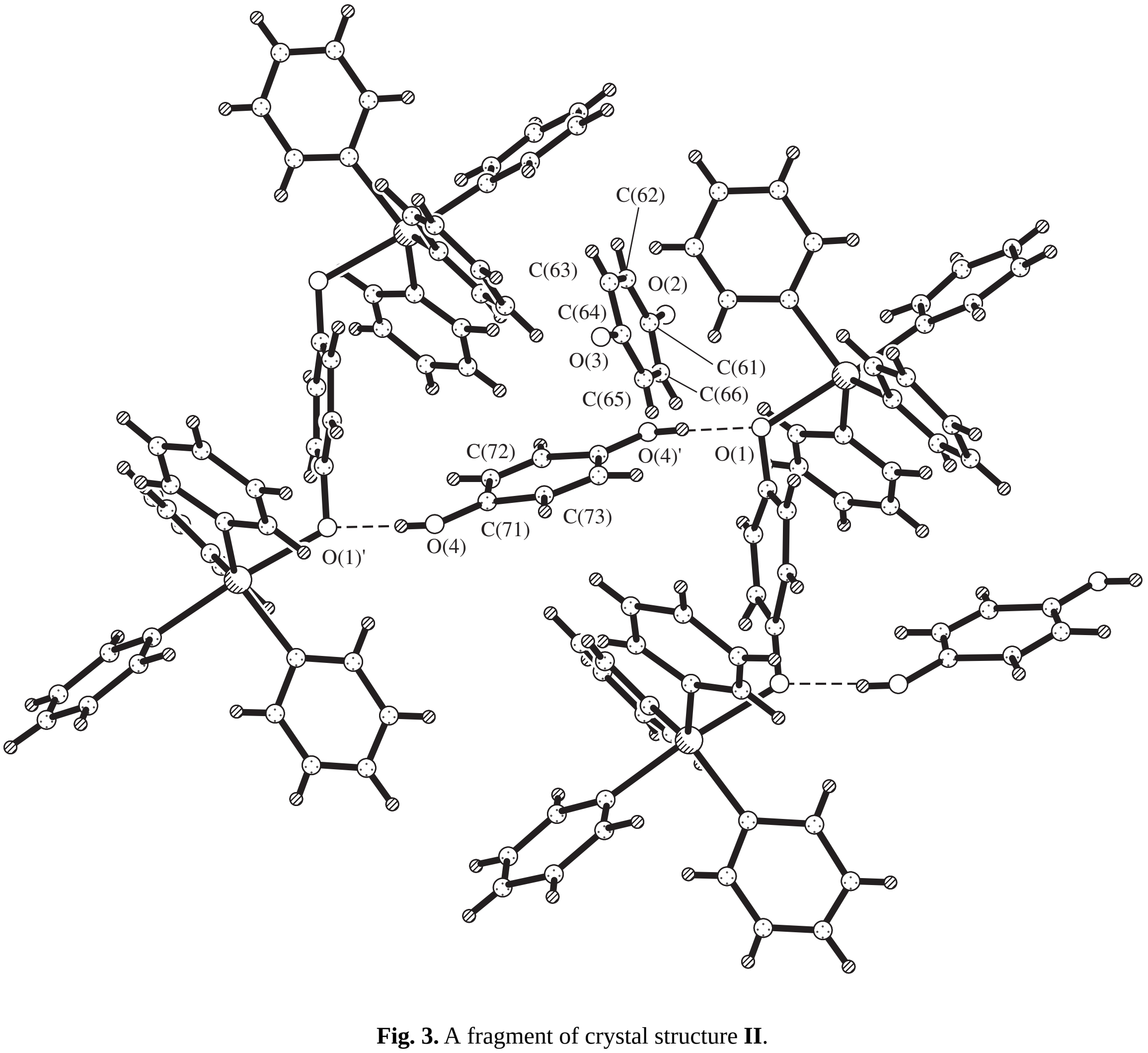

Fig. 3. A fragment of crystal structure **II**.

Table 1. Crystallographic data and details of data collection and refinement of structures **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{37}H_{33}O_2Sb$	$C_{72}H_{62}O_8Sb_2$
M	633.40	11298.72
T, K	296(2)	293(2)
Wave length, Å	MoK_α (0.71073)	MoK_α (0.71073)
Symmetry	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	10.2970(9)	10.066(1)
b, Å	28.436(3)	10.244(1)
c, Å	10.3228(9)	14.833(2)
α, deg	90	83.205(2)
β, deg	94.865(2)	87.309(3)
γ, deg	90	76.956(2)
V, Å^3	3011.6(5)	1479.2(4)
Z	4	1
ρ(calcd), g/cm^3	1.397	1.458
μ, mm^{-1}	0.947	0.971
F(000)	1296	660
Crystal size (shape), mm	Prism (0.45 × 0.45 × 0.45 mm)	Prism (0.20 × 0.25 × 0.30 mm)
Range of data collection for θ, deg	2.11–28.11	2.05–25.02
Ranges of reflection indices	$-13 \le h \le 13$, $-37 \le k \le 33$, $-13 \le l \le 10$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-16 \le l \le 17$
Measured reflections	18836	11578
Independent reflections	7318 (R_{int} = 0.0309)	5192 (R_{int} = 0.0336)
Reflections with $I > 2\sigma(I)$	5875	4342
Method of refinement	Full-matrix least-squares method for F^2	Full-matrix least-squares method for F^2
Number of refinement variables	366	373
GOOF	1.019	1.019
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0317$, $wR_2 = 0.0798$	$R_1 = 0.0360$, $wR_2 = 0.0850$
R factors for all reflections	$R_1 = 0.0419$, $wR_2 = 0.0834$	$R_1 = 0.0457$, $wR_2 = 0.0888$
Residual electron density (min/max), e/Å^3	–0.697/0.729	–576/1.342 (in the neighborhood of the Sb)

gen atoms of the initial phenol by the Ph_4Sb group, respectively:

$$Ph_5Sb + 1,3\text{-}(HO)_2C_6H_4$$

$$\longrightarrow Ph_4SbOC_6H_4(OH)\text{-}3 + PhH,$$

$$2Ph_5Sb + 4C_6H_4(HO)_2\text{-}1,4$$

$$\longrightarrow 1,4\text{-}(Ph_4SbO)_2C_6H_4 \cdot 3C_6H_4(OH)_2\text{-}1,4 + 2PhH.$$

These reactions start even at room temperature; however, for their termination, the reaction mixture must be heated at 90–100°C for 1 h.

The structures of the solvate of 1-(tetraphenylstiboxy)-3-oxybenzene $Ph_4SbOC_6H_4(OH)$-3 with toluene (**I**) and the 1,4-bis(tetraphenylstiboxy)benzene complex with hydroquinone 1,4-$(Ph_4SbO)_2C_6H_4 \cdot 3C_6H_4(HO)_2$ (**II**) were determined using X-ray diffraction analysis (Fig. 1).

The antimony-containing molecule in **II** contains two similar fragments joined by a twofold axis passing through the center of the hydroquinone group and bound to the Sb atoms through the C(52)–C(52*a*) and C(53)–C(53*a*) bonds (Fig. 2). In crystal **II**, the hydroquinone molecules join molecules of 1,4-bis(tetraphenylstiboxy)benzene via hydrogen bonds (Fig. 3).

Table 2. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\times 10^3$) in structures **I** and **II**

Atom	x	y	z	U_{eq}, Å^2	Atom	x	y	z	U_{eq}, Å^2
		I					**II**		
Sb	8447.7(1)	910.06(5)	7966.5(1)	37.16(6)	Sb	1802.9(2)	9877.3(2)	7243.9(1)	39.73(5)
O(1)	9085(2)	16426(5)	7719(1)	44.0(4)	O(1)	776(2)	11188(2)	8327(1)	45(1)
O(2)	8072(2)	26424(8)	4109(2)	62.1(5)	O(2)	8717(3)	3486(4)	7383(2)	122(1)
C(11)	6846(2)	10987(9)	6643(2)	43.8(5)	O(3)	3159(3)	4940(3)	7866(2)	106(1)
C(12)	6086(3)	1492(1)	6813(3)	56.2(6)	O(4)	1751(2)	3248(2)	8966(1)	57(1)
C(13)	5005(3)	1580(1)	5963(4)	72.6(9)	C(11)	1649(2)	11727(2)	6413(2)	41(1)
C(14)	4686(4)	1283(1)	4948(4)	80.0(1)	C(12)	1274(3)	11793(3)	5516(2)	54(1)
C(15)	5437(4)	892(1)	4759(4)	79(1)	C(13)	1191(3)	12949(3)	4950(2)	64(1)
C(16)	6501(3)	796(1)	5620(3)	61.7(7)	C(14)	1510(3)	14043(3)	5242(2)	68(1)
C(21)	7630(2)	205.8(8)	8179(2)	43.0(5)	C(15)	1905(3)	14002(3)	6114(2)	72(1)
C(22)	6309(3)	161(1)	8349(3)	57.2(7)	C(16)	1954(3)	12842(3)	6703(2)	63(1)
C(23)	5741(3)	–275(1)	8450(3)	68.7(8)	C(21)	3430(2)	9197(2)	8149(2)	43(1)
C(24)	6475(4)	−675(1)	8368(3)	70.1(9)	C(22)	4203(3)	10052(3)	8386(2)	54(1)
C(25)	7766(4)	−639(1)	8194(3)	68.4(8)	C(23)	5323(3)	9565(3)	8924(2)	61(1)
C(26)	8439(3)	–199(1)	8120(3)	54.7(7)	C(24)	5670(3)	8234(3)	9249(2)	69(1)
C(31)	8636(2)	1074.8(8)	9987(2)	40.0(5)	C(25)	4908(4)	7372(3)	9026(2)	80(1)
C(32)	8069(3)	783(1)	10847(3)	65.1(8)	C(26)	3795(3)	7851(3)	8461(2)	67(1)
C(33)	8172(4)	885(1)	12171(3)	82(1)	C(31)	45(2)	9069(2)	7313(2)	43(1)
C(34)	8855(4)	1269(1)	12629(3)	72.0(9)	C(32)	49(3)	7789(3)	7715(2)	65(1)
C(35)	9478(3)	1549(1)	11780(3)	65.9(8)	C(33)	–1142(4)	7299(3)	7721(2)	79(1)
C(36)	9373(3)	1450.7(9)	10469(2)	53.7(6)	C(34)	–2297(3)	8080(4)	7325(2)	74(1)
C(41)	10220(2)	689.3(8)	7271(2)	42.3(5)	C(35)	–2290(3)	9329(3)	6919(2)	67(1)
C(42)	11283(3)	626(1)	8159(3)	63.5(7)	C(36)	–1134(3)	9840(3)	6914(2)	56(1)
C(43)	12468(3)	484(1)	7760(4)	82(1)	C(41)	2847(2)	8706(2)	6159(2)	45(1)
C(44)	12609(4)	410(1)	6497(4)	81(1)	C(42)	4176(3)	8773(3)	5914(2)	57(1)
C(45)	11574(4)	461(1)	5594(4)	83(1)	C(43)	4851(3)	8156(3)	5202(2)	70(1)
C(46)	10361(3)	603(1)	5978(3)	63.2(8)	C(44)	4193(4)	7448(3)	4702(2)	77(1)
C(51)	9454(2)	1843.0(7)	6613(2)	38.7(5)	C(45)	2864(4)	7389(3)	4914(2)	74(1)
C(52)	10721(2)	1799.4(9)	6258(3)	49.5(6)	C(46)	2199(3)	8009(3)	5641(2)	60(1)
C(53)	11096(3)	2038(1)	5186(3)	55.1(7)	C(51)	407(2)	10569(2)	9139(2)	37(1)
C(54)	10250(3)	2323.3(9)	4447(2)	47.7(6)	C(52)	1251(2)	10322(3)	9887(2)	45(1)
C(55)	8985(2)	2368.8(8)	4791(2)	43.2(5)	C(53)	−850(3)	10225(3)	9276(2)	45(1)
C(56)	8587(2)	2125.4(8)	5858(2)	42.3(5)	C(61)	4508(3)	4504(3)	7769(2)	60(1)
C(1)	3360(10)	3337(2)	4402(7)	262(6)	C(62)	5133(4)	5178(3)	7084(2)	77(1)
C(61)	3942(8)	3138(2)	5521(6)	127(2)	C(63)	6520(4)	4834(3)	6972(3)	84(1)
C(62)	3172(5)	2958(2)	6420(8)	115(2)	C(64)	7290(3)	3834(4)	7540(2)	76(1)
C(63)	3752(7)	2769(2)	7549(8)	145(2)	C(65)	6639(4)	3192(4)	8232(3)	83(1)
C(64)	5058(7)	2751(2)	7829(7)	134(2)	C(66)	5252(3)	3528(3)	8344(2)	73(1)
C(65)	5807(5)	2945(2)	6939(8)	129(2)	C(71)	862(3)	4093(2)	9478(2)	43(1)
C(66)	5272(5)	3144(2)	5782(7)	123(2)	C(72)	1315(3)	5125(3)	9810(2)	52(1)
					C(73)	–470(3)	3984(3)	9685(2)	51(1)
					H(1)	1470(30)	2620(30)	8760(20)	70

Table 3. Separate bond lengths and angles in structures **I** and **II**

Bond	*d*, Å	Angle	ω, deg
I			
Sb–C(41)	2.113(2)	C(41)SbC(11)	120.2(1)
Sb–C(11)	2.120(2)	C(41)SbC(31)	112.86(9)
Sb–C(31)	2.130(2)	C(11)SbC(31)	125.22(9)
Sb–C(21)	2.191(2)	C(41)SbC(21)	96.48(9)
Sb–O(1)	2.205(1)	C(11)SbC(21)	90.65(9)
O(1)–C(51)	1.359(3)	C(31)SbC(21)	96.14(9)
O(2)–C(55)	1.368(3)	C(41)SbO(1)	88.12(8)
		C(11)SbO(1)	84.80(8)
		C(31)SbO(1)	84.39(7)
		C(21)SbO(1)	174.73(8)
		C(51)O(1)Sb	126.9(1)
II			
Sb–C(21)	2.107(2)	C(21)SbC(31)	123.5(1)
Sb–C(31)	2.110(3)	C(21)SbC(11)	119.7(1)
Sb–C(11)	2.114(2)	C(31)SbC(11)	115.29(9)
Sb–C(41)	2.205(3)	C(21)SbC(41)	94.03(9)
Sb–O(1)	2.276(2)	C(31)SbC(41)	95.8(1)
O(1)–C(51)	1.370(3)	C(11)SbC(41)	92.41(9)
O(2)–C(64)	1.415(4)	C(21)SbO(1)	86.10(8)
O(3)–C(61)	1.337(4)	C(31)SbO(1)	86.90(8)
O(4)–C(71)	1.367(3)	C(11)SbO(1)	84.66(8)
C(11)–C(16)	1.368(4)	C(41)SbO(1)	176.69(8)
C(11)–C(12)	1.389(4)	C(51)O(1)Sb	118.5(1)
C(12)–C(13)	1.357(4)	C(61)O(3)O(4)	117.2(2)
C(13)–C(14)	1.355(5)	C(71)O(4)O(3)	104.7(2)

The antimony atoms in compounds **I** and **II** are coordinated to the axial oxygen atoms to form a virtually undistorted trigonal bipyramid. The sums of bond angles in the equatorial planes are equal to 358.28(9)° (**I**) and 358.49(9)° (**II**), and the axial OSbC angles are equal to 174.73(8)° (**I**) and 176.69(8)° (**II**). The bond angles between the axial and equatorial substituents in structures **I** and **II** vary from 84.39(7)° to 96.48(9)° ($O_{ax}SbC_{eq} < 90°$, $C_{ax}SbC_{eq} > 90°$).

The equatorial Sb–C bond lengths are equal to 2.113(2)–2.130(2) Å (**I**) and 2.107(2)–2.114(2) Å (**II**). The lengths of the Sb–C$_{ax}$ bonds in **I** and **II** (2.191(2) and 2.205(3) Å) are greater than the statistically averaged lengths for structurally characterized aroxytetraphenylantimony compounds (2.184 Å) [5]. In **I**, the Sb–O$_{ax}$ distance (2.205(1) Å) is slightly longer than Sb–C$_{ax}$ and close to the Sb–O distances in other tetraphenylantimony phenolates (2.121(4)–2.221(4) Å) [5–8].

In **II**, the Sb–O bond (2.276(2) Å) is longer than the analogous bonds in known tetraphenylantimony phenolates. In our opinion, this is due to hydrogen bonds O(4)–H(1)··O(1)' between this O atom and the hydroxo group of a free hydroquinone molecule (O··O 2.795(3), O–H 0.85(3), O··H 1.94(3) Å; OHO angle, 178°) and the distribution of the electron density among a larger number of bonds. Location of the hydrogen atoms at O(2) and O(3) failed; however, the O(3)··O(4) (2.809(3) Å) and O(2)··O(1) (3.015(3) Å) distances indicate their weak interaction.

EXPERIMENTAL

Synthesis of 1-(tetraphenylstiboxy)-3-oxybenzene with toluene (I). A mixture of Ph$_5$Sb (1.00 g, 1.97 mmol), resorcin (0.22 g, 1.97 mmol), and toluene (15 ml) was heated at 100°C for 1 h and then cooled to room temperature; 5 ml of petroleum ether was then added, and the mixture obtained was cooled to –18°C. The crystals formed were filtered off and dried. The yield was 1.05 g (85%), mp = 159°C.

The complex of 1,4-bis(tetraphenylstiboxy)benzene with hydroquinone (II) was synthesized as above. The yield was 75%, mp = 105°C.

X-ray diffraction analysis of the natural-faceted single crystals of compounds **I** and **II** was carried out on a Bruker SMART-1000 CCD diffractometer. The data were collected in sets of 606 and 606, 435, and 230 scans at φ = 0°, 90°, 180°, and 270°C and φ = 0°, 90°, and 180°, respectively (ω-scan mode with a step of 0.3° and a counting time of 10 s for crystal **I** and 20 s for crystal **II**; crystal–detector distance 45 mm). Correction for absorption of X-rays by the samples was applied using the face indices.

The structures were solved by the direct methods and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and refined in the rider model.

The data collection and processing and the refinement of the unit cell parameters were performed using the SMART and SAINT Plus programs [9]. All the calculations for the determination and the refinement of structures **I** and **II** were carried out using the SHELXTL/PC programs [10].

Selected crystallographic parameters and the details of the structure refinement are presented in Table 1, coordinates and thermal parameters of atoms are given in Table 2, and their bond lengths and angles are listed in Table 3.

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