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STRUCTURE OF THE PRODUCTS OF THE REACTION OF 4-METHYLENE-1,3-DIOXOLAN-2-ONES WITH HYDRAZINES

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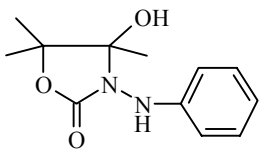
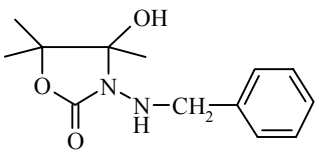
X-ray diffraction structural analysis was used to show the structure of one of the two products of the reaction of benzylhydrazine with 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one and of the only product of the reaction of phenylhydrazine with the same dioxolanone. Both compounds are derivatives of 3-amino-4-hydroxyoxazolidin-2-one.

Keywords: 3-amino-4-hydroxyoxazolidin-2-ones, hydrazines, 5-hydroxy-1,3,4-oxadiazin-2-ones, 4-methylene-1,3-dioxolan-2-ones, X-ray diffraction structural analysis.

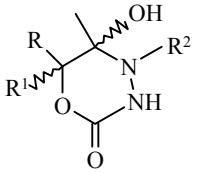
The reaction of 4-methylene-1,3-dioxolan-2-ones with hydrazines was examined in our previous work [1]. However, the identification of the products as derivatives of oxazolidin-2-one **3** or 1,2,3-oxadiazin-2-one **A** remained unclear. Neither the ^{1}H NMR spectral data or the combined set of IR and ^{1}H NMR spectral and mass spectrometric data provided an unequivocal answer. This question was solved by X-ray diffraction structural analysis.* Both phenyl derivative **3a** (Fig. 1, Tables 1 and 2) and benzyl derivative **3b** proved to be five-membered oxazolidin-2-ones.



3a



3b



A

Five-membered heterocycle O(1)–C(2)–N(3)–C(4)–C(5) in **3a** has *envelope* conformation. The deviation of C(4) from the N(3)–C(2)–0(1)–C(5) plane is -0.555 Å (the deviations of the atoms from the indicated plane are ±0.003 Å). The dihedral angle between this plane and the plane traversing N(3)–C(4)–C(5) is 34.1°. The C(10)···C(15) dihedral angle between the plane of the five-membered heterocycle and the plane of the phenyl substituent is 89.9°, while the torsion angles C(2)–N(3)–N(9)–C(10) and N(3)–N(9)–C(10)–C(11) are -76.2° and -29.1°, respectively, indicating significant twist of these molecular fragments relative to each

* See also our communication [2].

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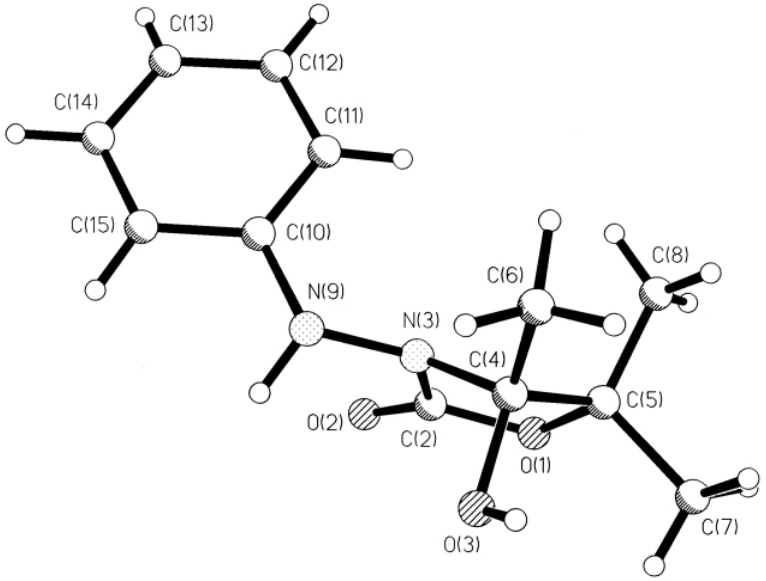

Fig. 1. Structure of oxazolidinone **3a**.

other. Elongation of the C(4)–C(5) single bond to 1.552(5) Å was noted, probably related to the presence of substituents at these atoms giving rise to steric hindrance. According to Goldberg [3] and Claremon [4], the length of such a single bond does not exceed 1.536 Å in related compounds without steric hindrance. The other geometric parameters (bond lengths *d* and bond angles ω) in this molecule are ordinary and have standard values [5]. A rather strong intermolecular hydrogen bond is noted in the crystal for O(3)–H(3O)···O(2) (1/2 + *x*, 3/2 - *y*, *z*) with parameters: O(3)···O(2), 2.706(4); O(3)–H(3O), 0.90(4); H(3O)···O(2), 1.84(4) Å; angle O(3)–H(3O)···O(2), 138(3)°. This hydrogen bond links the molecules into infinite chains along the *a*-axis (Fig. 2). We should note that the hydrogen atom at N(9) shown in Fig. 1 does not form hydrogen bonds or have shortened intra- or intermolecular nonbonding contacts. The coordinates for all the atoms, isotropic temperature parameters for the hydrogen atoms, and the equivalent temperature parameters for the non-hydrogen atoms are given in Table 3.

The five-membered heterocycle O(1)–C(2)–N(3)–C(4)–C(5) in oxazolidinone **3b** (Fig. 3, Tables 4 and 5) has *half-chair* conformation. The deviations of C(4) and C(5) from the O(1)–C(2)–N(3) plane are 0.276 and -0.203 Å, respectively, while the analogous heterocycle in the phenyl derivative has *envelope* conformation. The C(11)···C(16) dihedral angle between the plane of the five-membered heterocycle and plane of the phenyl substituent is 62.2°, while the torsion angles C(2)–N(3)–N(9)–C(10), -68.1°; N(3)–N(9)–C(10)–C(11), -62.6°,

TABLE 1. Bond Lengths in Oxazolidinone **3a**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O(1)–C(2)	1.334(4)	C(5)–C(8)	1.500(7)	N(9)–C(10)	1.421(5)
O(1)–C(5)	1.492(5)	C(5)–C(7)	1.515(6)	C(4)–C(6)	1.494(6)
O(2)–C(2)	1.206(4)	C(10)–C(11)	1.374(5)	C(11)–C(12)	1.384(6)
O(3)–C(4)	1.395(5)	C(10)–C(15)	1.398(5)	C(12)–C(13)	1.384(6)
N(3)–C(2)	1.367(5)	N(3)–N(9)	1.392(4)	C(13)–C(14)	1.360(7)
C(4)–C(5)	1.552(5)	N(3)–C(4)	1.459(4)	C(14)–C(15)	1.384(6)

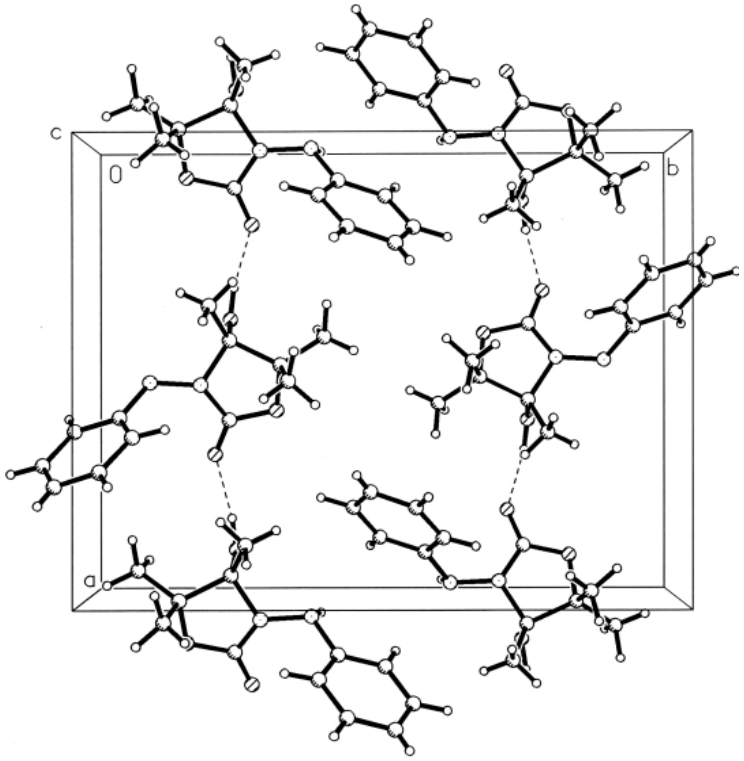

Fig. 2. Packing of molecules in the crystal of oxazolidinone **3a** projection *ab* (the intermolecular O–H···O hydrogen bonds are given by dashed lines).

N(9)–C(10)–C(11)–C(12), -78.8° indicate a mutual twisting of these molecular fragments. As in phenyl derivative **3a**, elongation of the C(4)–C(5) single bond is noted to 1.545(5) Å, related to the steric hindrance arising between the substituents attached to these two atoms. The other geometric parameters (bond lengths *d* and bond angles ω) in this molecule have standard values [5].

TABLE 2. Bond Angles in Oxazolidinone **3a**

Angle	ω, deg.	Angle	ω, deg.	Angle	ω, deg.
C(2)–O(1)–C(5)	108.6(3)	O(1)–C(5)–C(4)	101.9(3)	N(3)–C(4)–C(5)	97.5(3)
C(2)–N(3)–N(9)	121.4(3)	C(8)–C(5)–C(4)	114.4(4)	C(6)–C(4)–C(5)	116.2(4)
C(2)–N(3)–C(4)	109.7(3)	C(7)–C(5)–C(4)	114.2(4)	C(11)–C(10)–N(9)	121.3(3)
N(9)–N(3)–C(4)	120.4(3)	C(11)–C(10)–C(15)	120.0(3)	C(15)–C(10)–N(9)	118.7(3)
N(3)–N(9)–C(10)	115.2(3)	O(1)–C(2)–N(3)	109.3(3)	C(10)–C(11)–C(12)	119.9(3)
O(2)–C(2)–O(1)	124.2(3)	O(3)–C(4)–N(3)	105.4(3)	C(11)–C(12)–C(13)	119.9(4)
O(2)–C(2)–N(3)	126.4(3)	O(3)–C(4)–C(6)	112.7(3)	C(14)–C(13)–C(12)	120.3(4)
O(1)–C(5)–C(8)	106.3(3)	N(3)–C(4)–C(6)	112.9(3)	C(13)–C(14)–C(15)	120.5(4)
O(1)–C(5)–C(7)	107.1(3)	O(3)–C(4)–C(5)	110.7(3)	C(14)–C(15)–C(10)	119.3(4)
C(8)–C(5)–C(7)	111.9(4)				

TABLE 3. Coordinates ($\times 10^4$), Isotropic Temperature Parameters for the Hydrogen Atoms, and Equivalent Temperature Parameters for the Non-hydrogen Atoms in Oxazolidinone **3a**

Atom	*x*	*y*	*z*	*U*
O(1)	9154(2)	8244(1)	2225(5)	34(1)
O(2)	8179(2)	7191(2)	1016(6)	45(1)
O(3)	11121(2)	7449(2)	1044(6)	35(1)
N(3)	9703(2)	7009(2)	3067(6)	30(1)
N(9)	9756(2)	6169(2)	2817(7)	34(1)
C(2)	8944(3)	7454(2)	1979(7)	30(1)
C(4)	10655(3)	7491(2)	3253(7)	29(1)
C(5)	10130(3)	8330(2)	3626(7)	35(1)
C(6)	11359(3)	7207(3)	5173(8)	38(1)
C(7)	10731(4)	9037(3)	2594(9)	49(1)
C(8)	9795(4)	8493(3)	6105(9)	49(1)
C(10)	9011(2)	5723(2)	4140(7)	28(1)
C(11)	8626(3)	6016(2)	6226(7)	31(1)
C(12)	7935(3)	5552(2)	7521(8)	36(1)
C(13)	7624(3)	4798(2)	6702(9)	40(1)
C(14)	8012(3)	4503(2)	4650(8)	37(1)
C(15)	8711(3)	4955(2)	3342(8)	33(1)
H(3O)	11803(35)	7517(22)	1367(75)	28(10)
H(9N)	9757(31)	6032(24)	1252(89)	35(11)
H(61)	11645(39)	6729(32)	4430(106)	63(15)
H(62)	11850(43)	7599(29)	5464(100)	58(15)
H(63)	11029(27)	7156(21)	6766(72)	21(9)
H(71)	11415(37)	9091(28)	3523(99)	57(14)
H(72)	10437(42)	9525(39)	3095(131)	89(19)
H(73)	10901(37)	8912(28)	1049(107)	51(14)
H(81)	9300(47)	8928(36)	6124(112)	79(17)
H(82)	9430(33)	8124(29)	6935(89)	41(12)
H(83)	10401(33)	8600(23)	6956(78)	34(11)
H(11)	8794(29)	6551(26)	6700(77)	39(11)
H(12)	7676(28)	5746(21)	8930(72)	24(10)
H(13)	7247(34)	4574(28)	7418(93)	44(14)
H(14)	7818(32)	3948(27)	4072(88)	50(13)
H(15)	8953(26)	4786(22)	1832(77)	24(9)

TABLE 4. Bond Lengths in Oxazolidinone **3b**

Bond	*d*, Å	Bond	*d*, Å
O(1)–C(2)	1.352(4)	N(3)–N(9)	1.402(4)
O(1)–C(5)	1.483(4)	N(3)–C(4)	1.475(4)
O(2)–C(2)	1.220(4)	N(9)–C(10)	1.479(5)
O(3)–C(4)	1.421(4)	C(4)–C(8)	1.506(5)
N(3)–C(2)	1.336(5)	C(4)–C(5)	1.545(5)
C(5)–C(7)	1.508(5)	C(12)–C(13)	1.397(6)
C(5)–C(6)	1.538(5)	C(13)–C(14)	1.355(6)
C(10)–C(11)	1.517(5)	C(14)–C(15)	1.373(7)
C(11)–C(16)	1.375(5)	C(15)–C(16)	1.396(6)
C(11)–C(12)	1.389(6)		

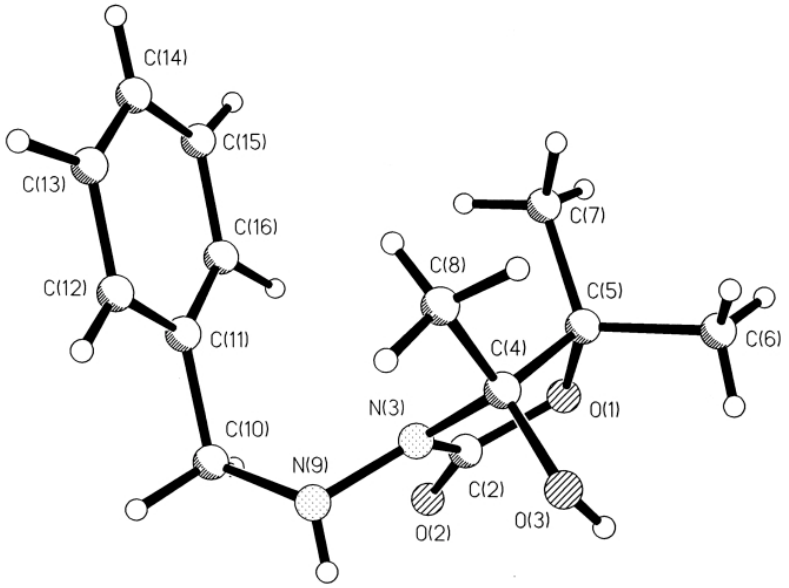

Fig. 3. Structure of Oxazolidinone **3b**.

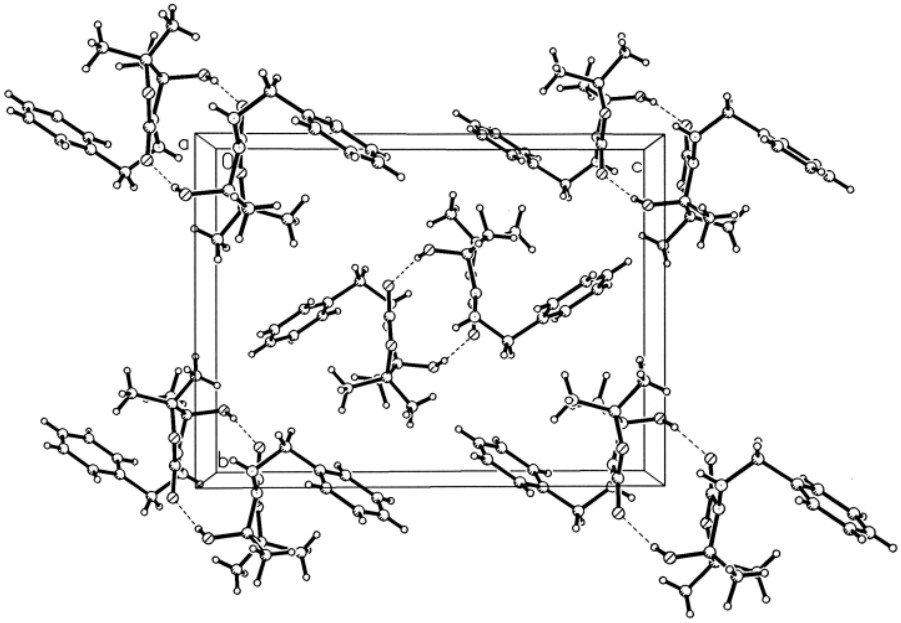

Fig. 4. Molecular packing in the crystal of oxazolidinone **3b**, projection *bc*
(the intermolecular O–H···O hydrogen bonds are indicated by dashed lines).

The hydroxyl group hydrogen atom in the crystal of **3b** participates in the formation of an intermolecular hydrogen bond O(3)–H(3O)···O(2) (-*x*, 1 - *y*, 1 - *z*) [O(3)···O(2), 2.799(2); O(3)–H(3O), 0.99(2); H(3O)···O(2), 1.82(2) Å, angle O(3)–H(3O)···O(2), 166(2)°]. The hydrogen bonds connect the molecules into centrosymmetric dimers (Fig. 4). We should note that the hydrogen atom at N(9) (Fig. 3) does not form any hydrogen bonds or participate in any shortened intra- or intermolecular nonbonding contacts (Table 6).

TABLE 5. Bond Angles in Oxazolidinone **3b**

Angle	ω, deg.	Angle	ω, deg.	Angle	ω, deg.
C(2)–O(1)–C(5)	108.0 (3)	O(1)–C(5)–C(4)	103.4 (3)	O(3)–C(4)–C(5)	114.0 (3)
C(2)–N(3)–N(9)	124.9 (3)	C(7)–C(5)–C(4)	114.6 (3)	N(3)–C(4)–C(5)	97.9 (3)
C(2)–N(3)–C(4)	112.5 (3)	C(6)–C(5)–C(4)	113.5 (3)	C(8)–C(4)–C(5)	116.5 (3)
N(9)–N(3)–C(4)	119.5 (3)	N(9)–C(10)–C(11)	110.4 (3)	O(1)–C(5)–C(7)	106.5 (3)
N(3)–N(9)–C(10)	112.7 (3)	C(16)–C(11)–C(12)	119.3 (4)	C(12)–C(11)–C(10)	120.0 (4)
O(2)–C(2)–N(3)	127.6 (4)	C(16)–C(11)–C(10)	120.7 (4)	C(11)–C(12)–C(13)	120.1 (4)
O(2)–C(2)–O(1)	122.5 (4)	O(3)–C(4)–N(3)	110.0 (3)	C(14)–C(13)–C(12)	119.7 (5)
N(3)–C(2)–O(1)	109.9 (3)	O(3)–C(4)–C(8)	105.8 (3)	C(13)–C(14)–C(15)	121.3 (5)
O(1)–C(5)–C(6)	106.6 (3)	N(3)–C(4)–C(8)	112.5 (3)	C(14)–C(15)–C(16)	119.4 (5)
C(7)–C(5)–C(6)	111.4 (3)			C(11)–C(16)–C(15)	120.3 (4)

TABLE 6. Coordinates ($\times 10^4$), Isotropic Temperature Parameters for the Hydrogen Atoms, and Equivalent Temperature Parameters for the Non-hydrogen Atoms in Oxazolidinone **3b**

Atom	*x*	*y*	*z*	*U*
O(1)	608(4)	6090(2)	4072(2)	37(1)
O(2)	49(4)	4239(2)	4003(2)	41(1)
O(3)	-3076(4)	6824(2)	5051(2)	33(1)
N(3)	-2477(4)	5513(2)	3978(2)	27(1)
N(9)	-4103(5)	4796(3)	4022(2)	33(1)
C(2)	-588(6)	5189(4)	4014(2)	31(1)
C(4)	-2706(5)	6702(3)	4184(2)	28(1)
C(5)	-634(5)	7098(3)	3947(2)	30(1)
C(6)	252(8)	7994(4)	4542(3)	43(1)
C(7)	-485(7)	7430(4)	3039(3)	39(1)
C(8)	-4442(7)	7228(3)	3713(3)	35(1)
C(10)	-4356(7)	4068(3)	3276(2)	39(1)
C(11)	-4763(6)	4760(3)	2490(2)	32(1)
C(12)	-6640(6)	5187(4)	2314(3)	40(1)
C(13)	-7012(7)	5832(4)	1594(3)	49(1)
C(14)	-5538(8)	6026(4)	1065(3)	54(1)
C(15)	-3667(8)	5619(4)	1229(3)	49(1)
C(16)	-3288(7)	4968(3)	1945(3)	40(1)
H(3O)	-1889(70)	6528(40)	5363(32)	82(17)
H(9N)	-3874(50)	4466(29)	4474(24)	26(11)
H(61)	235(56)	7751(32)	5077(26)	43(12)
H(62)	1596(53)	8160(28)	4414(21)	28(10)
H(63)	-845(79)	8614(46)	4555(34)	95(18)
H(71)	-1145(60)	6856(37)	2641(28)	61(13)
H(72)	979(52)	7480(26)	2925(21)	27(10)
H(73)	-1270(56)	8124(36)	2875(25)	53(12)
H(81)	-5799(52)	6943(27)	3920(21)	29(9)
H(82)	-4277(49)	7171(28)	3094(25)	33(10)
H(83)	-4482(57)	7963(37)	3857(27)	55(13)
H(101)	-5749(55)	3592(30)	3380(24)	46(11)
H(102)	-3156(55)	3653(30)	3186(23)	42(12)
H(12)	-7603(54)	5008(30)	2674(23)	37(11)
H(13)	-8409(55)	6029(29)	1381(25)	40(11)
H(14)	-5652(59)	6402(32)	628(28)	43(13)
H(15)	-2614(53)	5764(29)	895(24)	36(11)
H(16)	-1976(60)	4720(33)	2120(26)	49(12)

EXPERIMENTAL

All the calculations were carried out on an IBM PC/AT-586 computer using the SHELXTL PLUS and SHELXL-93 packages [6].

Colorless crystals of phenyl derivative **3a** were obtained by slow crystallization from acetonitrile over three days. The orthorhombic crystals of $C_{12}H_{16}N_2O_3$ were studied at -80°C: a = 12.830(6), b = 16.461(10), c = 5.697(4) Å; V = 1203(1) Å^3; d_{calc} = 1.304 g/cm^3; Z = 4; space group $Pna2_1$. The unit cell parameters and intensities of 1459 reflections were measured on a Syntex P2(1) automatic four-circle diffractometer using λMo$K\alpha$ radiation, graphite monochromator, and θ/2θ scanning to θ_{max} = 27°. The structure was determined by the direct method and refined by the full-matrix method of least squares anistropically for the non-hydrogen atoms. The hydrogen atoms were localized objectively in the Fourier difference map and refined isotropically. The final divergence factors wR_2 = 0.1408 over 1407 independent reflections (R_1 = 0.049 over 980 independent reflections with $I > 2\sigma(I)$).

Colorless crystals of benzyl derivative **3b** were obtained by slow crystallization from acetonitrile over three days. The monoclinic crystals of $C_{13}H_{18}N_2O_3$ were measured at -60°C: a = 6.775(4), b = 12.013(5), c = 15.923(8) Å; β = 92.53(4)°; V = 1295(1) Å^3; d_{calc} = 1.284 g/cm^3; Z = 4; space group $P2_1/c$. The unit cell parameters and intensities of 2892 reflections were measured on a Syntex P2(1) automatic four-circle diffractometer using λMo$K\alpha$ radiation, graphite monochromator, and θ/2θ scanning to θ_{max} = 27. The structure was solved by the direct method and refined by the full-matrix method of least squares anisotropically for the non-hydrogen atoms. The hydrogen atoms were located objectively in the Fourier difference map and refined isotropically. The final divergence factors wR_2 = 0.156 over 2573 independent reflections (R_1 = 0.075 over 1126 independent reflections with $I > 2\sigma(I)$).

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