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HETEROCYCLES CONTAINING A BRIDGE NITROGEN ATOM.* 11.** RECYCLIZATION OF 5-METHYLOXAZOLO[3,2-*a*]PYRIDINIUM CATION UNDER THE ACTION OF NUCLEOPHILES CONTAINING NH_2 GROUP. CRYSTAL STRUCTURE OF 3-(*p*-NITROPHENYL)-1,4-DIHYDROPYRIDO-[2,1-*c*]-*as*-TRIAZINIUM PERCHLORATE

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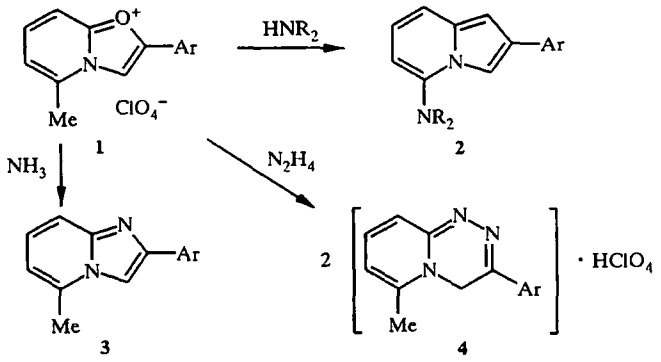
Reactions of 5-methyl-2-(p-nitrophenyl)oxazolo[3,2-a]pyridinium perchlorate with ammonia and hydrazine, in contrast to the reaction with secondary amines, do not produce indolizines. The reaction with ammonia produces 5-methyl-2-(p-nitrophenyl)imidazo[1,2-a]pyridine; with hydrazine, 3-(p-nitrophenyl)-1,4-dihydropyrido[2,1-c]-as-triazinium semiperchlorate (2 moles of base per one mole of acid). The structure of the latter is solved by X-ray structural studies.

Earlier we observed [2-4] that the reaction of 5-methyloxazolo[3,2-*a*]pyridinium **1** derivatives with secondary amines involves an unusual recyclization of the oxazole ring into pyrrole system to produce an unknown subclass of 5-aminoindolizines **2**. Lower homologs of oxazolopyridine that do not contain methyl group in the 5-position react with secondary amines to open the six-membered ring [4, 5]. However, the reaction with ammonia



1-4 Ar = *p*-$NO_2C_6H_4$

* Dedicated to Professor Henk van der Plas on his 70th birthday.

** For No. 9, see [1].

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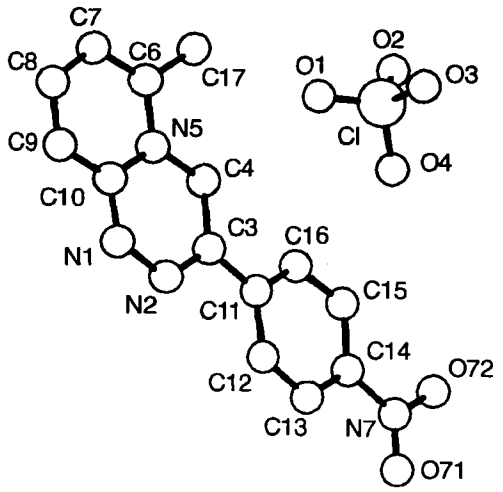

Fig. 1. Geometric arrangement of atoms in molecule of compound **4**. The first digit of the atom numbers in Tables 1-3 denotes whether the atom belongs to the first or second independent molecule of composition $2[C_{14}H_{12}N_4O_2]\cdot HClO_4$.

[6, 7] and secondary amines [7] transforms the oxazole ring into imidazole. The reaction of cations **1** with nucleophiles containing the NH_2 group has not been studied. The products of such reactions could be either 5-substituted indolizines or other heterocycles, for example, a series of imidazopyridines.

We found that salt **1** (Ar = *p*-$NO_2C_6H_4$) does not react with aniline and *p*-anisidine. After prolonged boiling of the reagents, starting material is recovered. The reaction of **1** with primary amines RNH_2 (R = butyl, *sec*-butyl, benzyl) in the amine or in acetonitrile medium is accompanied by considerable tarring. The reaction mixture gives a negative Ehrlich test (a color test for the presence of indolizines [8]) and no neutral compounds can be isolated from it. On the other hand, the reaction with ammonia gas in DMSO occurs quite smoothly, producing a practically quantitative yield of imidazopyridine **3**. (Let us note that the current method for preparing **3** according to Chichibabin [9] gives a low yield and involves complicated isolation.)

The reaction with hydrazine produced a red crystalline compound that occured to be 3-(*p*-nitrophenyl)-1,4-dihydropyrido[2,1-*c*]-*as*-triazinium perchlorate **4** (according to X-ray structural studies); the base:$HClO_4$ ratio being 2:1. The PMR spectrum of **4** exhibits singlets for the methylene and methyl groups and broad signals for the protons of the pyridine and aryl moieties.

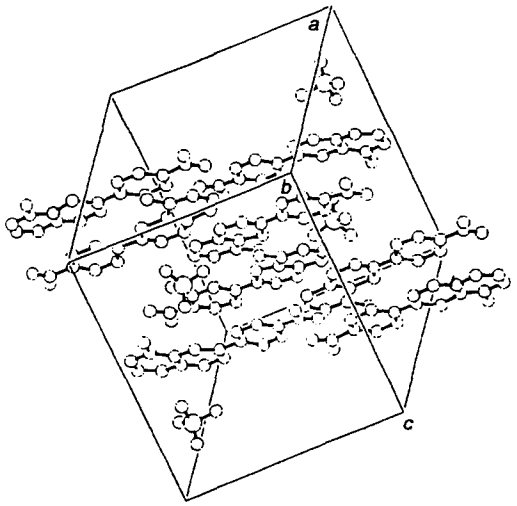

Fig. 2. Packing of molecules in crystal of compound **4**.

TABLE 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Parameters ($U_{eq} \times 10^3$) in Structure **4**

Atom	x	y	z	U_{eq}
1	2	3	4	5
Cl	7627(1)	1436(1)	498(1)	49(1)
$O_{(1)}$	7926(3)	2208(4)	1190(3)	144(3)
$O_{(2)}$	8100(3)	1480(4)	-83(4)	172(3)
$O_{(3)}$	6610(3)	1570(4)	-56(3)	139(2)
$O_{(4)}$	7720(4)	694(4)	1049(4)	179(3)
$N_{(11)}$	2773(2)	-1681(2)	-3214(2)	43(1)
$N_{(12)}$	2828(2)	-2624(2)	-3063(2)	34(1)
$C_{(13)}$	3568(3)	-2940(3)	-2316(3)	35(2)
$C_{(14)}$	4379(3)	-2380(3)	-1499(2)	23(1)
$N_{(15)}$	4260(2)	-1382(2)	-1779(2)	24(1)
$C_{(16)}$	5021(3)	-792(3)	-1195(3)	37(2)
$C_{(17)}$	4883(3)	117(4)	-1394(3)	55(2)
$C_{(18)}$	4023(3)	427(3)	-2214(3)	45(2)
$C_{(19)}$	3338(3)	-155(3)	-2852(3)	30(2)
$C_{(110)}$	3453(3)	-1085(3)	-2589(3)	41(2)
$C_{(111)}$	3617(3)	-3936(3)	-2233(3)	36(2)
$C_{(112)}$	2837(3)	-4497(3)	-2842(3)	38(2)
$C_{(113)}$	2900(3)	-5420(4)	-2767(3)	51(2)
$C_{(114)}$	3709(3)	-5830(3)	-2008(3)	40(2)
$C_{(115)}$	4467(3)	-5295(3)	-1295(3)	48(2)
$C_{(116)}$	4428(3)	-4341(3)	-1403(3)	40(2)
$C_{(117)}$	5928(3)	-1162(3)	-328(3)	37(2)
$N_{(17)}$	3765(3)	-6818(3)	-1872(3)	62(2)
$O_{(171)}$	3138(2)	-7257(2)	-2545(2)	68(1)
$O_{(172)}$	4469(2)	-7144(3)	-1197(2)	73(2)
$N_{(21)}$	-1360(2)	1082(2)	-4974(2)	50(2)
$N_{(22)}$	-1274(2)	156(3)	-4925(3)	53(2)
$C_{(23)}$	-552(2)	-218(3)	-4171(2)	22(1)
$C_{(24)}$	306(3)	299(3)	-3360(3)	27(1)
$N_{(25)}$	99(2)	1279(2)	-3444(2)	31(1)
$C_{(26)}$	756(3)	1868(3)	-2707(3)	32(2)
$C_{(27)}$	625(3)	2810(4)	-2838(3)	52(2)
$C_{(28)}$	-162(3)	3132(3)	-3677(3)	46(2)
$C_{(29)}$	-833(3)	2589(3)	-4393(3)	49(2)
$C_{(210)}$	-680(3)	1644(3)	-4274(3)	38(2)
$C_{(211)}$	-528(3)	-1229(3)	-4173(3)	27(1)
$C_{(212)}$	-1315(3)	-1742(3)	-4885(3)	48(2)
$C_{(213)}$	-1259(3)	-2677(4)	-4915(3)	51(2)
$C_{(214)}$	-467(3)	-3117(3)	-4144(3)	34(2)
$C_{(215)}$	313(3)	-2598(3)	-3405(3)	49(2)
$C_{(216)}$	286(3)	-1669(3)	-3419(3)	43(2)
$C_{(217)}$	1605(3)	1426(3)	-1816(3)	45(2)
$N_{(27)}$	-391(3)	-4124(3)	-4175(3)	58(2)
$O_{(271)}$	-1084(2)	-4519(3)	-4870(2)	77(2)
$O_{(272)}$	293(2)	-4514(2)	-3502(2)	62(1)
$H_{(14A)}$	4273(20)	-2429(23)	-721(21)	32(11)
$H_{(14B)}$	5056(23)	-2566(27)	-1432(24)	51(13)
$H_{(17)}$	5367(20)	548(24)	-998(20)	23(11)
$H_{(18)}$	3927(25)	994(28)	-2251(27)	62(14)
$H_{(19)}$	2758(22)	65(25)	-3390(23)	46(12)
$H_{(112)}$	2261(24)	-4223(28)	-3403(26)	67(14)
$H_{(113)}$	2322(18)	-5837(20)	-3207(18)	3(8)
$H_{(115)}$	5075(23)	-5586(26)	-794(23)	48(12)
$H_{(116)}$	4968(23)	-3928(25)	-1003(24)	50(12)

TABLE 1 (continued)

1	2	3	4	5
$H_{(11A)}$	6322(21)	-1544(27)	-635(21)	42(11)
$H_{(11B)}$	5735(22)	-1527(26)	108(23)	44(12)
$H_{(11C)}$	6361(28)	-612(34)	140(30)	104(18)
$H_{(24A)}$	354(22)	59(26)	-2650(24)	46(13)
$H_{(24B)}$	978(29)	91(32)	-3539(30)	98(17)
$H_{(27)}$	1079(20)	3169(22)	-2388(20)	18(10)
$H_{(28)}$	-176(27)	3660(32)	-3898(29)	84(16)
$H_{(29)}$	-1381(23)	2748(27)	-4969(25)	56(13)
$H_{(212)}$	-1863(28)	-1470(33)	-5292(30)	107(17)
$H_{(213)}$	-1794(27)	-2921(31)	-5419(28)	82(16)
$H_{(215)}$	829(23)	-2829(26)	-2937(24)	46(12)
$H_{(216)}$	853(27)	-1345(31)	-2884(28)	82(16)
$H_{(21A)}$	2047(28)	1868(33)	-1421(30)	101(17)
$H_{(21B)}$	1999(22)	1154(25)	-2022(23)	45(12)
$H_{(21C)}$	1269(21)	1152(23)	-1443(21)	29(11)

It should be noted that the first members of the 3-aryl-1,4-dihydropyrido[2,1-*c*]-*as*-triazine subclass were synthesized by Bradsher et al. [7] *via* the reaction of 2-chloro-N-phenacylpyridinium salts with hydrazine. The authors [7] isolated the ordinary perchlorate, which reacted with bases to convert into a compound containing 2 moles of base per 1 mole of acid (an analog of **4**). The structure of that compound was explained by proposing the situation of two base molecules around one proton with symmetric hydrogen bonds. Our results indicate that the unit cell of **4** actually contains two crystallographically independent molecules (see Fig. 2 and Tables 2 and 3). Table 2 shows that the interatomic distances in the framework of both molecules are similar although not identical. Furthermore, such pairs of molecules are situated practically parallel within the unit cell (Fig. 2) so excluding the

TABLE 2. Bond Lengths *d* (Å) in Molecule of Compound **4**

Bond	*d*	Bond	*d*
$Cl–O_{(1)}$	1,453(5)	$Cl–O_{(3)}$	1,372(4)
$Cl–O_{(2)}$	1,298(6)	$Cl–O_{(4)}$	1,322(6)
$N_{(11)}–C_{(110)}$	1,346(5)	$N_{(21)}–C_{(210)}$	1,362(5)
$N_{(11)}–N_{(12)}$	1,393(5)	$N_{(21)}–N_{(22)}$	1,358(5)
$N_{(12)}–C_{(13)}$	1,257(4)	$N_{(22)}–C_{(23)}$	1,282(4)
$C_{(13)}–C_{(111)}$	1,461(6)	$C_{(23)}–C_{(211)}$	1,478(6)
$C_{(13)}–C_{(14)}$	1,520(5)	$C_{(23)}–C_{(24)}$	1,516(5)
$C_{(14)}–N_{(15)}$	1,505(5)	$C_{(24)}–N_{(25)}$	1,458(6)
$N_{(15)}–C_{(110)}$	1,343(4)	$N_{(25)}–C_{(210)}$	1,374(4)
$N_{(15)}–C_{(16)}$	1,381(5)	$N_{(25)}–C_{(26)}$	1,397(5)
$C_{(16)}–C_{(17)}$	1,357(7)	$C_{(26)}–C_{(27)}$	1,393(7)
$C_{(16)}–C_{(117)}$	1,497(5)	$C_{(26)}–C_{(217)}$	1,513(5)
$C_{(17)}–C_{(18)}$	1,397(5)	$C_{(27)}–C_{(28)}$	1,363(5)
$C_{(18)}–C_{(19)}$	1,345(5)	$C_{(28)}–C_{(29)}$	1,350(6)
$C_{(19)}–C_{(110)}$	1,404(6)	$C_{(29)}–C_{(210)}$	1,399(7)
$C_{(111)}–C_{(112)}$	1,382(5)	$C_{(211)}–C_{(212)}$	1,400(5)
$C_{(111)}–C_{(116)}$	1,420(5)	$C_{(211)}–C_{(216)}$	1,392(5)
$C_{(112)}–C_{(113)}$	1,354(7)	$C_{(212)}–C_{(213)}$	1,371(7)
$C_{(113)}–C_{(114)}$	1,372(5)	$C_{(213)}–C_{(214)}$	1,387(5)
$C_{(114)}–C_{(115)}$	1,397(6)	$C_{(214)}–C_{(215)}$	1,416(5)
$C_{(114)}–N_{(17)}$	1,457(6)	$C_{(214)}–N_{(27)}$	1,478(6)
$C_{(115)}–C_{(116)}$	1,401(7)	$C_{(215)}–C_{(216)}$	1,359(7)
$N_{(17)}–O_{(172)}$	1,184(4)	$N_{(27)}–O_{(272)}$	1,210(4)
$N_{(17)}–O_{(171)}$	1,208(5)	$N_{(27)}–O_{(271)}$	1,234(4)

Table 3. Bond Angles ω (deg.) in Molecule of Compound **4**

Angle	ω	Angle	ω
$O_{(2)}$–Cl–$O_{(4)}$	119,2(4)	$O_{(2)}$–Cl–$O_{(1)}$	109,1(3)
$O_{(2)}$–Cl–$O_{(3)}$	110,2(3)	$O_{(3)}$–Cl–$O_{(1)}$	103,6(3)
$O_{(4)}$–Cl–$O_{(3)}$	106,7(3)	$O_{(4)}$–Cl–$O_{(1)}$	106,9(3)
$N_{(12)}$–$N_{(11)}$–$C_{(110)}$	123,8(3)	$N_{(22)}$–$N_{(21)}$–$C_{(210)}$	122,7(3)
$C_{(13)}$–$N_{(12)}$–$N_{(11)}$	118,2(3)	$C_{(23)}$–$N_{(22)}$–$N_{(21)}$	119,6(3)
$N_{(12)}$–$C_{(13)}$–$C_{(111)}$	115,7(3)	$N_{(22)}$–$C_{(23)}$–$C_{(211)}$	115,9(3)
$N_{(12)}$–$C_{(13)}$–$C_{(14)}$	125,9(4)	$N_{(22)}$–$C_{(23)}$–$C_{(24)}$	124,7(4)
$C_{(111)}$–$C_{(13)}$–$C_{(14)}$	118,4(3)	$C_{(211)}$–$C_{(23)}$–$C_{(24)}$	119,2(3)
$N_{(15)}$–$C_{(14)}$–$C_{(13)}$	110,2(3)	$N_{(25)}$–$C_{(24)}$–$C_{(23)}$	110,5(3)
$C_{(110)}$–$N_{(15)}$–$C_{(16)}$	121,5(4)	$C_{(210)}$–$N_{(25)}$–$C_{(26)}$	119,1(4)
$C_{(110)}$–$N_{(15)}$–$C_{(14)}$	120,7(3)	$C_{(210)}$–$N_{(25)}$–$C_{(24)}$	121,4(3)
$C_{(16)}$–$N_{(15)}$–$C_{(14)}$	117,8(3)	$C_{(26)}$–$N_{(25)}$–$C_{(24)}$	119,3(3)
$C_{(17)}$–$C_{(16)}$–$N_{(15)}$	118,1(3)	$C_{(27)}$–$C_{(26)}$–$N_{(25)}$	119,5(3)
$C_{(17)}$–$C_{(16)}$–$C_{(117)}$	122,2(4)	$C_{(27)}$–$C_{(26)}$–$C_{(217)}$	123,8(3)
$N_{(15)}$–$C_{(16)}$–$C_{(117)}$	119,5(4)	$N_{(25)}$–$C_{(26)}$–$C_{(217)}$	116,7(4)
$C_{(16)}$–$C_{(17)}$–$C_{(18)}$	120,0(4)	$C_{(26)}$–$C_{(27)}$–$C_{(28)}$	118,7(4)
$C_{(19)}$–$C_{(18)}$–$C_{(17)}$	121,9(4)	$C_{(29)}$–$C_{(28)}$–$C_{(27)}$	123,8(5)
$C_{(18)}$–$C_{(19)}$–$C_{(110)}$	117,0(3)	$C_{(28)}$–$C_{(29)}$–$C_{(210)}$	117,3(4)
$N_{(11)}$–$C_{(110)}$–$N_{(15)}$	120,8(4)	$N_{(21)}$–$C_{(210)}$–$N_{(25)}$	120,0(4)
$N_{(11)}$–$C_{(110)}$–$C_{(19)}$	118,1(3)	$N_{(21)}$–$C_{(210)}$–$C_{(29)}$	118,3(3)
$N_{(15)}$–$C_{(110)}$–$C_{(19)}$	120,9(4)	$N_{(25)}$–$C_{(210)}$–$C_{(29)}$	121,5(3)
$C_{(112)}$–$C_{(111)}$–$C_{(116)}$	117,9(4)	$C_{(212)}$–$C_{(211)}$–$C_{(216)}$	120,1(4)
$C_{(112)}$–$C_{(111)}$–$C_{(13)}$	122,6(3)	$C_{(212)}$–$C_{(211)}$–$C_{(23)}$	121,6(3)
$C_{(116)}$–$C_{(111)}$–$C_{(13)}$	118,8(3)	$C_{(216)}$–$C_{(211)}$–$C_{(23)}$	118,2(3)
$C_{(113)}$–$C_{(112)}$–$C_{(111)}$	122,0(4)	$C_{(213)}$–$C_{(212)}$–$C_{(211)}$	121,0(4)
$C_{(112)}$–$C_{(113)}$–$C_{(114)}$	120,5(4)	$C_{(212)}$–$C_{(213)}$–$C_{(214)}$	118,5(4)
$C_{(113)}$–$C_{(114)}$–$C_{(115)}$	120,1(4)	$C_{(213)}$–$C_{(214)}$–$C_{(215)}$	119,9(4)
$C_{(113)}$–$C_{(114)}$–$N_{(17)}$	121,6(4)	$C_{(213)}$–$C_{(214)}$–$N_{(27)}$	119,0(3)
$C_{(115)}$–$C_{(114)}$–$N_{(17)}$	118,2(3)	$C_{(215)}$–$C_{(214)}$–$N_{(27)}$	120,7(3)
$C_{(114)}$–$C_{(115)}$–$C_{(116)}$	119,4(4)	$C_{(214)}$–$C_{(215)}$–$C_{(216)}$	121,0(4)
$C_{(115)}$–$C_{(116)}$–$C_{(111)}$	119,4(4)	$O_{(272)}$–$N_{(27)}$–$C_{(214)}$	119,4(3)
$O_{(171)}$–$N_{(17)}$–$C_{(114)}$	115,8(3)	$C_{(271)}$–$N_{(27)}$–$C_{(214)}$	116,5(3)

possibility of formation of linear hydrogen bonds in the plane containing both bicyclic fragments. Unfortunately, the low quality of the crystals did not enable localization of the hydrogen atom responsible for formation of such hydrogen bond. A possible solution of this problem would be to perform an analogous experiment using neutron diffraction of a deuterated sample (for example, treating **4** with deuterated perchloric acid). This would enable the hydrogen atom to be located.

Yet another feature of the structure of **4** is the distinct alternation of single and double bonds in the pyridine moiety. We previously noted this phenomenon [1, 2] in various members of a series of azolopyridines with a bridge nitrogen atom.

Thus, reactions of 5-methyloxazolopyridines with nucleophiles containing the NH_2 group do not produce indolizine derivatives. Apparently opened species containing rather acidic amino or hydrazino protons undergo tautomerism and form phenacyl group that further reacts intramolecularly with ring closure involving the N-containing nucleophile to give 5- and 6-membered rings.

EXPERIMENTAL

Reaction of 5-Methyl-2-(*p*-nitrophenyl)oxazolo[3,2-*a*]pyridinium (1) with Ammonia. DMSO was saturated with gaseous ammonia and in 20 ml of the obtained solution perchlorate of **1** (0.1 g, 0.3 mmol) was suspended. The solution was stored for 7 days at room temperature and poured into water. The solid was filtered

off. Yield 0.07 g (98%) of 5-methyl-2-(*p*-nitrophenyl)imidazo[1,2-*a*]pyridine (**3**) that had properties (mp, IR and PMR spectra, chromatographic behavior) identical to those of an authentic sample [1].

Reaction of 5-Methyl-2-(*p*-nitrophenyl)oxazolo[3,2-*a*]pyridinium (1) with Hydrazine. Solution of compound **1** (0.1 g, 0.3 mmol) in acetonitrile (5 ml) was treated with hydrazine hydrate (0.3 ml). The solution was stored for 7 days at room temperature. The red crystals were filtered off. Yield 0.07 g (78%) of **4**; mp 268°C. PMR spectrum (400 MHz, DMSO-d_6): 8.29 (2H, m, *p*-NO_2Ph), 8.14 (2H, m, *p*-NO_2Ph), 7.78 (1H, dd, 8-H), 7.02 (1H, d, 9-H, J = 9.25 Hz), 6.97 (1H, d, J = 8.9 Hz, 7-H), 5.32 (2H, s, CH_2), 2.68 ppm (3H, s, CH_3).

X-ray Structural Studies of Compound 4 were performed on a CAD-4 single-crystal diffractometer [10] using λ MoKα-radiation and a graphite monochromator. The unit cell parametrs were determined and refined using 25 reflections in the range of 13–15° θ. Crystals of **4** belong to the monoclinic syngony (space group $P2_1/c$) with the unit cell parametrs a = 14.560(4), b = 14.618(9), c = 14.579(5) Å; β = 114.69(3)°; Z = 8; and V = 2820(2) Å^3.

The structure was solved by direct methods using the SHELXS-97 programs [11] and refined by anisotropic least-squares methods for the nonhydrogen atoms. The positions of all hydrogen atoms of the heterocycles (except the proton on $N_{(1)}$, see above) were located in a difference Fourier electron-density synthesis. The final R-factor was 0.1088 for 4480 independent reflections with $I > 2\sigma(I)$.

Table 1 contains the atomic coordinates and the isotropic thermal parameters that are equivalent to the corresponding anisotropic ones. Tables 2 and 3 list the interatomic distances and bond angles. Figure 1 shows the arrangement of atoms and their numbering. Figure 2 shows the molecular packing [13].

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REFERENCES

1. E. V. Babaev, V. B. Rybakov, S. G. Zhukov, and I. A. Orlova, *Khim. Geterotsikl. Soedin.*, No. 4, 542 (1999).
2. E. V. Babaev, A. V. Efimov, S. G. Zhukov, and V. B. Rybakov, *Khim. Geterotsikl. Soedin.*, No. 7, 983 (1998).
3. E. V. Babaev and A. V. Efimov, *Khim. Geterotsikl. Soedin.*, No. 7, 998 (1997).
4. E. V. Babaev, A. V. Efimov, D. A. Maiboroda, and K. Jug, *Eur. J. Org. Chem.*, No. 1, 193 (1998).
5. D. A. Maiboroda, E. V. Babaev, and L. V. Goncharenko, *Khim. Farm. Zh.*, No. 6, 24 (1998).
6. E. V. Babaev, K. Yu. Pasichnichenko, and D. A. Maiboroda, *Khim. Geterotsikl. Soedin.*, No. 3, 397 (1997).
7. C. K. Bradsher, R. D. Brandau, J. E. Boilek, and T. L. Hough, *J. Org. Chem.*, **34**, 2129 (1969).
8. W. Flitsch, in: *Comprehensive Heterocyclic Chemistry*, Vol. 4, A. R. Katritzky and C. W. Rees (eds.), Pergamon, Oxford (1984), p. 443.
9. F. Mattu and E. Marongiu, *Rend. Semin. Fac. Sci. Univ. Cagliari*, No. 34, 190 (1964).
10. Enraf – Nonius CAD-4 Software, Version 5.0, Enraf – Nonius, Delft, Netherlands (1989).
11. G. M. Sheldrick, *SHELXS-97. Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).
12. G. M. Sheldrick, *SHELXL-97. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
13. A. L. Spek, *PLUTON-92. Molecular Graphics Program*, University of Utrecht, Netherlands (1992).