STRUCTURE
OF ORGANIC COMPOUNDS

X-ray Mapping in Heterocyclic Design:
XIII. Structure of Substituted Tetrahydroquinolines

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Abstract—The structures of 4-methyl-2-chloro-5,6,7,8-tetrahydroquinoline [$a = 8.138(2)$ Å, $b = 11.127(4)$ Å, $c = 11.234(2)$ Å, $\beta = 111.30(2)°$, $Z = 4$, space group $P2_1/c$, 4-methyl-2-methoxy-5,6,7,8- tetrahydroquinoline [$a = 5.7651(16)$ Å, $b = 8.530(2)$ Å, $c = 10.455(3)$ Å, $\alpha = 73.76(2)°$, $\beta = 86.95(2)°$, $\gamma = 83.97(2)°$, $Z = 2$, space group $P\bar{1}$, 4-methyl-2-(4-chlorophenacyl)-5,6,7,8-tetrahydro-1H-quinolin-2-one [$a = 8.873(2)$ Å, $b = 17.137(2)$ Å, $c = 24.515(4)$ Å, $Z = 8$, space group $Pbn2_1$], and 2-(4-chlorophenyl)-5-methyl-6,7,8,9-tetrahydrooxazolo[3.2-a]quinolin-10-ylium perchlorate [$a = 8.110(6)$ Å, $b = 17.818(7)$ Å, $c = 17.721(5)$ Å, $\beta = 100.46(4)°$, $Z = 4$, space group $P2_1/c$] are studied by single-crystal X-ray diffraction. The structures are solved by direct methods and refined by the full-matrix least-squares procedures in the anisotropic approximation to $R = 0.0581, 0.0667, 0.0830,$ and 0.0607, respectively. © 2004 MAIK "Nauka/Interperiodica".

INTRODUCTION

This study continues our structural investigation of heterocyclic compounds that are able to undergo various rearrangements, in particular, to enter into cyclization reactions [1–13]. As was done in our previous works, we perform X-ray diffraction analysis of all the intermediates and final products of multistage cyclization reactions and rearrangements. 2-Pyridone derivatives are structural precursors in many of the systems studied earlier.

In this work, we studied a series of transformations from 4-methyl-5,6,7,8-tetrahydro-1H-quinolin-2-one (**I**) into 2-(4-chlorophenyl)-5-methyl-6,7,8,9-tetrahy- drooxazolo[3.2-a]quinolin-10-ylium perchlorate (**V**) (Scheme 1).

The data on the molecular structures of compounds **II**–**V** discussed in this paper are not available in the Cambridge Structural Database (version 11.02) [14].

EXPERIMENTAL

Compound **I** was synthesized and characterized in our earlier work [11]. This paper reports the synthesis and structures of compounds **II**–**V**.

4-Methyl-2-chloro-5,6,7,8-tetrahydroquinoline (II). Our attempt to convert pyridone **I** into chloropyridine **II**
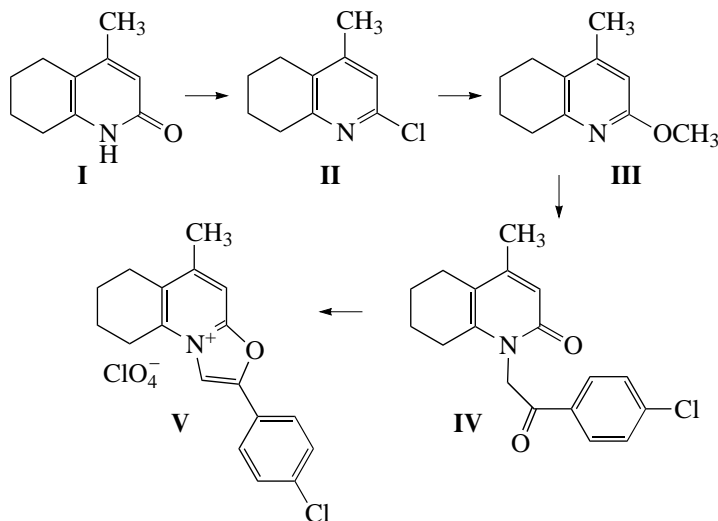
Scheme 1.

Table 1. Crystal data, data collection, and refinement parameters for the crystal structures of compounds **II–V**

Empirical formula	$C_{10}H_{12}NCl$ (**II**)	$C_{11}H_{15}NO$ (**III**)	$C_{20}H_{21}N_2O_2Cl$ (**IV**)	$C_{18}H_{17}NO_5Cl_2$ (**V**)
Molecular weight	181.66	177.24	356.84	398.23
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$Pbn2_1$	$P2_1/c$
a, Å	8.138(2)	5.7651(16)	8.873(2)	8.110(6)
b, Å	11.127(4)	8.530(2)	17.137(2)	17.818(7)
c, Å	11.234(2)	10.455(3)	24.515(4)	17.721(5)
α, deg	90	73.76(2)	90	90
β, deg	111.30(2)	86.95(2)	90	100.46(4)
γ, deg	90	83.79(2)	90	90
V, Å^3	947.8(4)	490.6(2)	3727.7(13)	1807.7(17)
Z	4	2	8	4
ρ_{calcd}, g/cm^3	1.273	1.200	1.272	1.463
$\mu(K_\alpha)$, cm^{-1}	3.46	0.77	19.33	34.97
θ range, deg	2.67–25.97	2.03–25.95	3.60–69.78	5.54–69.77
Index ranges	$-10 \le h \le 9$	$-7 \le h \le 1$	$0 \le h \le 10$	$-7 \le h \le 7$
	$0 \le k \le 13$	$-10 \le k \le 10$	$0 \le k \le 20$	$0 \le k \le 18$
	$0 \le l \le 13$	$0 \le l \le 12$	$0 \le l \le 29$	$0 \le l \le 17$
Crystal size, mm	$0.26 \times 0.29 \times 0.30$	$0.31 \times 0.32 \times 0.35$	$0.22 \times 0.24 \times 0.29$	$0.27 \times 0.29 \times 0.30$
Number of reflections measured	1892	1158	3342	3271
Number of unique reflections	1799	1140	3342	3271
Number of reflections used in the least-squares refinement/number of parameters refined	1799/114	1140/121	3342/456	3271/237
GooF	1.020	1.026	0.914	0.998
R_1/wR_2 [$I \ge 2\sigma(I)$]	0.0581/0.1474	0.0667/0.1793	0.0830/0.1991	0.0607/0.1604
$\Delta\rho_{max}/\Delta\rho_{min}$, eÅ^{-3}	0.284/−0.232	0.172/−0.151	0.592/−0.208	0.303/−0.325

Table 2. Bond lengths d (Å) in structure **II**

Bond	d	Bond	d
N(1)–C(2)	1.301(4)	C(5)–C(10)	1.384(4)
N(1)–C(10)	1.344(4)	C(5)–C(6)	1.516(4)
C(2)–C(3)	1.357(4)	C(6)–C(7)	1.468(7)
C(2)–Cl(2)	1.754(3)	C(7)–C(8)	1.350(8)
C(3)–C(4)	1.377(4)	C(8)–C(9)	1.496(8)
C(4)–C(5)	1.388(4)	C(9)–C(10)	1.510(5)
C(4)–C(11)	1.502(4)		

Table 3. Bond angles ω (deg) in structure **II**

Angle	ω	Angle	ω
C(2)–N(1)–C(10)	116.1(2)	C(10)–C(5)–C(6)	120.9(3)
N(1)–C(2)–C(3)	126.5(3)	C(4)–C(5)–C(6)	120.5(3)
N(1)–C(2)–Cl(2)	115.4(2)	C(7)–C(6)–C(5)	114.3(4)
C(3)–C(2)–Cl(2)	118.1(2)	C(8)–C(7)–C(6)	119.9(5)
C(2)–C(3)–C(4)	117.8(3)	C(7)–C(8)–C(9)	120.5(5)
C(3)–C(4)–C(5)	118.2(3)	C(8)–C(9)–C(10)	111.9(4)
C(3)–C(4)–C(11)	119.9(3)	N(1)–C(10)–C(5)	122.8(3)
C(5)–C(4)–C(11)	121.9(3)	N(1)–C(10)–C(9)	114.7(3)
C(10)–C(5)–C(4)	118.5(2)	C(5)–C(10)–C(9)	122.5(3)

simply through boiling in POCl$_3$ failed. The procedure described in [15] requires heating to 180°C in a sealed ampule, which is impracticable. Therefore, we worked out an original path of synthesis of compound **II**. Weighed portions of **I** (10 g) and benzyltrimethylammonium chloride (11 g) were refluxed in POCl$_3$ (33 ml)

until the formation of HCl ceased (within about 5 h). A hot homogeneous dark solution was poured in a glass with ice. Activated carbon was added, and the solution was stirred and filtered off. The light solution thus prepared was neutralized with solid sodium hydrogen carbonate to pH = 7, and the precipitate was filtered off. A

Table 4. Bond lengths d (Å) in structure **III**

Bond	d	Bond	d
N(1)–C(2)	1.328(5)	C(5)–C(10)	1.337(5)
N(1)–C(10)	1.368(4)	C(5)–C(6)	1.537(4)
C(2)–O(1)	1.363(4)	C(6)–C(7)	1.531(6)
C(2)–C(3)	1.381(6)	C(7)–C(8)	1.444(7)
C(3)–C(4)	1.369(4)	C(8)–C(9)	1.501(5)
C(4)–C(5)	1.422(5)	C(9)–C(10)	1.514(5)
C(4)–C(11)	1.492(6)	O(1)–C(1)	1.402(6)

Table 5. Bond angles ω (deg) in structure **III**

Angle	ω	Angle	ω
C(2)–N(1)–C(10)	115.3(3)	C(4)–C(5)–C(6)	118.5(3)
N(1)–C(2)–O(1)	118.7(4)	C(7)–C(6)–C(5)	111.2(3)
N(1)–C(2)–C(3)	124.8(3)	C(8)–C(7)–C(6)	115.1(3)
O(1)–C(2)–C(3)	116.5(3)	C(7)–C(8)–C(9)	113.2(4)
C(4)–C(3)–C(2)	118.7(3)	C(8)–C(9)–C(10)	112.4(3)
C(3)–C(4)–C(5)	117.9(4)	C(5)–C(10)–N(1)	124.5(3)
C(3)–C(4)–C(11)	120.7(3)	C(5)–C(10)–C(9)	122.8(3)
C(5)–C(4)–C(11)	121.4(3)	N(1)–C(10)–C(9)	112.6(3)
C(10)–C(5)–C(4)	118.7(3)	C(2)–O(1)–C(1)	118.1(3)
C(10)–C(5)–C(6)	122.8(3)		

Table 6. Bond lengths d (Å) in structure **IV**

Bond	d	Bond	d
Cl(1)–C(17)	1.728(9)	C(7)–C(8)	1.438(15)
N(1)–C(2)	1.361(10)	C(8)–C(9)	1.471(13)
N(1)–C(10)	1.422(10)	C(9)–C(10)	1.513(11)
N(1)–C(12)	1.456(10)	C(12)–C(13)	1.509(11)
C(2)–O(2)	1.232(11)	C(13)–O(13)	1.215(9)
C(2)–C(3)	1.417(12)	C(13)–C(14)	1.495(10)
C(3)–C(4)	1.355(11)	C(14)–C(19)	1.390(10)
C(4)–C(5)	1.459(12)	C(14)–C(15)	1.402(10)
C(4)–C(11)	1.591(14)	C(15)–C(16)	1.375(10)
C(5)–C(10)	1.376(12)	C(16)–C(17)	1.376(10)
C(5)–C(6)	1.498(11)	C(17)–C(18)	1.377(11)
C(6)–C(7)	1.552(15)	C(18)–C(19)	1.389(11)

white powder obtained was recrystallized from chloroform. The yield was 8.6 g (78%). The melting point was equal to 35–40°C. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.82 (m, 4H, 6-CH$_2$ + 7-CH$_2$), 2.19 (s, 3H, 4-CH$_3$), 2.60 (t, 2H, 5-CH$_2$), 2.78 (t, 2H, 8-CH$_2$), 6.95 (s, 1H, 3-CH).

4-Methyl-2-methoxy-5,6,7,8-tetrahydroquinoline (III). No indications of the reaction (precipitation of sodium chloride) were observed in our attempt to prepare methoxy pyridine **III** from chloropyridine **II** according to the procedure described in [16]. An analysis of the reaction mixture showed that the product was not formed and the starting substance remained without changes. We proposed an original procedure with the use of a high-boiling inert solvent that dissolves both the initial substance and sodium methylate and is water-mixable for the facilitation of the product isolation. Diglym satisfies these conditions. Metallic sodium (2.8 g) was dissolved in absolute methanol (20 ml), the excess methanol was distilled off, and a solution of compound **II** (7.8 g) in absolute diglyme (40 ml) was added. The mixture was heated at 120°C for 3 h. This process was accompanied by a thickening of the mixture because of the copious precipitate formation. The reaction mixture was poured into water and stirred. The precipitate was filtered off and washed with water. The white powder obtained was recrystallized from chloroform. The yield was 6.1 g (80%). The melting point was equal to 35–40°C. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.80 (m, 4H, 6-CH$_3$ + 7-CH$_2$), 2.15 (s, 3H, 4-CH$_3$), 2.54 (t, 2H, 5-CH$_2$), 2.70 (t, 2H, 8-CH$_2$), 3.78 (s, 3H, OCH$_3$), 6.35 (s, 1H, 3-CH).

4-Methyl-2-(4-chlorophenacyl)-5,6,7,8-tetrahydro-1*H*-quinolin-2-one (IV). Compound **IV** was synthesized according to a modified procedure described in [16]. Weighed portions of compound **III** (3 g) and 4-chlorophenacyl bromide (4 g) were refluxed in CH$_3$CN (20 ml) for 5 h. As a result, a poorly soluble compound, namely, 4-chlorophenacyl bromide, dissolved. The degree of conversion was controlled by thin-layer chromatography (hexane : ethyl acetate = 1 : 1). For both initial substances, we obtained R_f = 0.72, and, for the product, R_f = 0.1. Upon cooling of the solution, colorless crystals of the product containing solvate CH$_3$CN molecules precipitated. Only minor amounts of the product remained in the mother liquor. The yield was 2 g (40%). The melting point was equal to 163–165°C. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.75 (m, 4H, 6-CH$_2$ + 7-CH$_2$), 2.13 (s, 3H, 4-CH$_3$), 2.50 (m, 4H, 5-CH$_2$ + 8-CH$_2$), 5.45 (s, 2H, NCH$_2$CO), 6.15 (s, 1H, 3-CH), 7.55, 8.10 (dd, 4H, *Ar*).

2-(4-Chlorophenyl)-5-methyl-6,7,8,9-tetrahydro-oxazolo[3.2-*a*]quinolin-10-ylium perchlorate (V). The synthesis of compound **V** was also performed according to the procedure worked out earlier in [16]. Compound **IV** (1.2 g) was dissolved in concentrated H$_2$SO$_4$ (12 ml) and allowed to stand for a night. The solution was poured into a 3% HClO$_4$ solution (100 ml). The precipitate was left in the solution for a night and then filtered off and washed with water. The white powder obtained was recrystallized from CH$_3$CN. The yield was 1.5 g (98%). The melting point was 300°C (with explosion). ^{1}H NMR (DMSO-d_6, δ,
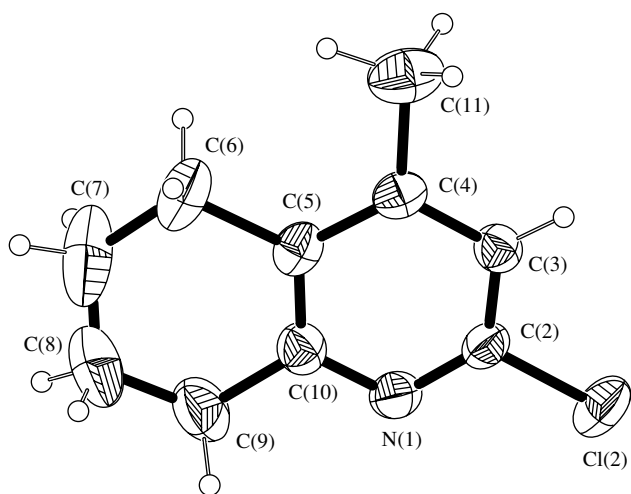
Fig. 1. Molecular structure and atomic numbering for compound **II**. Hereafter, the ellipsoids of thermal vibrations are shown at the 50% probability level.
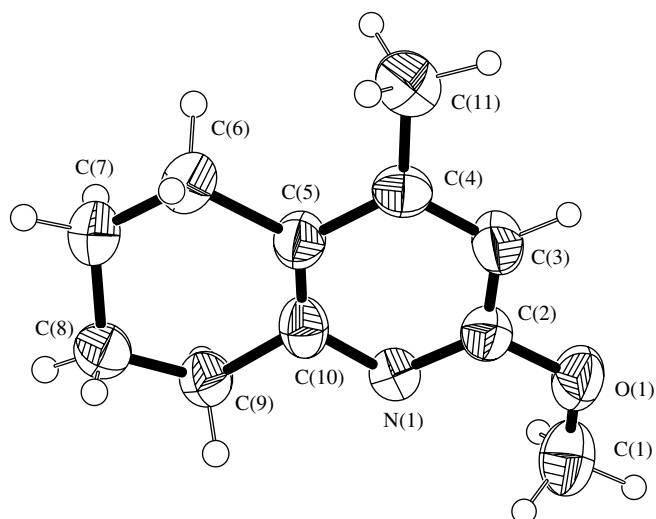

Fig. 2. Molecular structure and atomic numbering for compound **III**.

ppm): 1.95 (m, 2H, 7-CH$_2$), 2.05 (m, 2H, 8-CH$_2$), 2.58 (s, 3H, 5-CH$_3$), 2.85 (t, 2H, 6-CH$_2$), 3.15 (t, 2H, 9-CH$_2$), 7.63–7.66, 8.03–8.06 (dd, 4H, *Ar*), 8.11 (s, 1H, 4-CH), 9.37 (s, 1H, 1-CH).

X-ray Diffraction Experiment

For single crystals of compounds **II** and **III**, the experimental intensities were measured on a CAD4 diffractometer [17] (λMoK_α, graphite monochromator) at room temperature. The unit cell parameters were determined and refined using 25 reflections in the θ range 12°–15°. For compounds **IV** and **V**, the experiment was performed on a CAD4 diffractometer (λCuK_α, graphite monochromator). The unit cell parameters were determined and refined using 25 reflections in the θ range 25°–30°.

Since the crystals of the compounds studied were small in size and had small linear absorption coefficients ($\mu R \leq 0.4$), the experimental data were not corrected for absorption. The primary processing of the sets of diffraction data was performed with the WinGX program package [18]. All the subsequent calculations were performed with the SHELX97 program package [19]. The crystal structures were determined by direct methods. All the non-hydrogen atoms were refined in the anisotropic approximation of thermal parameters.

The main parameters of the X-ray diffraction experiments and crystal data for the compounds studied are summarized in Table 1. The interatomic distances and bond angles are listed in Tables 2–9. The molecular structures with atomic numberings are shown in Figs. 1–4. The drawings were obtained with the ORTEP-3 program [20, 21].

Crystal data for the compounds studied are deposited in the Cambridge Structural Database (deposit nos. 231747–231750).

RESULTS AND DISCUSSION

In molecule **II** (Fig. 1), the N(1)···C(10) six-membered ring is planar within 0.011 Å. The Cl(2), C(6), C(9), and C(11) atoms lie in the plane of this ring. The C(7) and C(8) atoms deviate from this plane by 0.124 and –0.290 Å, respectively. The thermal ellipsoids of

Table 7. Bond angles ω (deg) in structure **IV**

| Angle	ω	Angle	ω
C(2)–N(1)–C(10)	124.7(8)	C(5)–C(10)–N(1)	117.0(7)
C(2)–N(1)–C(12)	115.1(7)	C(5)–C(10)–C(9)	125.1(8)
C(10)–N(1)–C(12)	120.1(7)	N(1)–C(10)–C(9)	117.9(8)
O(2)–C(2)–N(1)	120.7(8)	N(1)–C(12)–C(13)	112.3(7)
O(2)–C(2)–C(3)	123.9(9)	O(13)–C(13)–C(14)	122.8(7)
N(1)–C(2)–C(3)	115.1(8)	O(13)–C(13)–C(12)	120.7(8)
C(4)–C(3)–C(2)	125.5(10)	C(14)–C(13)–C(12)	116.4(7)
C(3)–C(4)–C(5)	116.0(9)	C(19)–C(14)–C(15)	119.7(8)
C(3)–C(4)–C(11)	125.8(10)	C(19)–C(14)–C(13)	123.3(7)
C(5)–C(4)–C(11)	118.0(9)	C(15)–C(14)–C(13)	117.0(7)
C(10)–C(5)–C(4)	121.6(8)	C(16)–C(15)–C(14)	122.1(9)
C(10)–C(5)–C(6)	118.5(9)	C(15)–C(16)–C(17)	118.3(9)
C(4)–C(5)–C(6)	119.8(9)	C(16)–C(17)–C(18)	119.6(9)
C(5)–C(6)–C(7)	112.3(9)	C(16)–C(17)–Cl(1)	123.1(8)
C(8)–C(7)–C(6)	119.4(13)	C(18)–C(17)–Cl(1)	117.2(8)
C(7)–C(8)–C(9)	109.4(12)	C(17)–C(18)–C(19)	123.4(10)
C(8)–C(9)–C(10)	114.6(10)	C(18)–C(19)–C(14)	116.7(9)
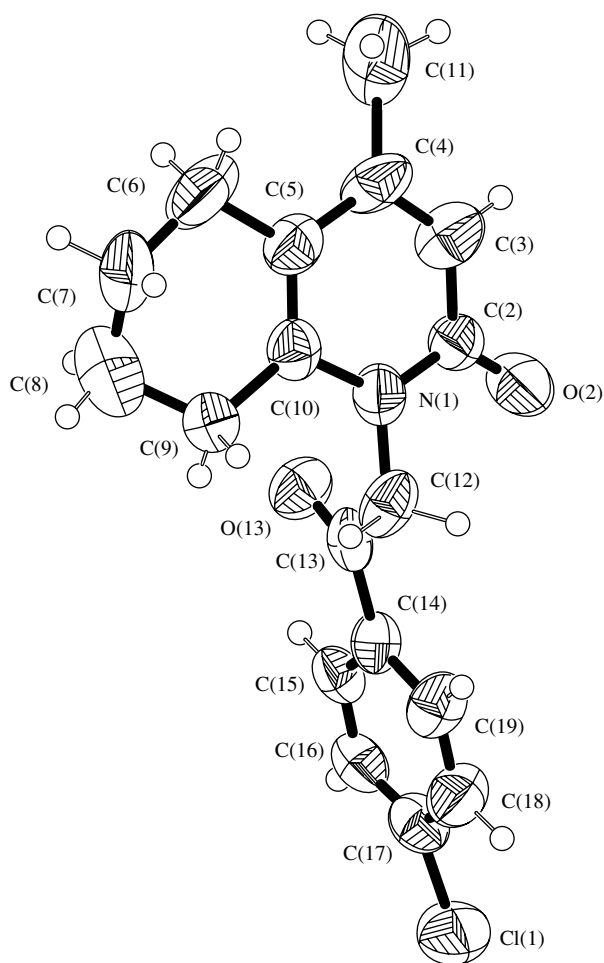
Fig. 3. Molecular structure and atomic numbering for compound **IV**. Acetonitrile solvate molecules are omitted.
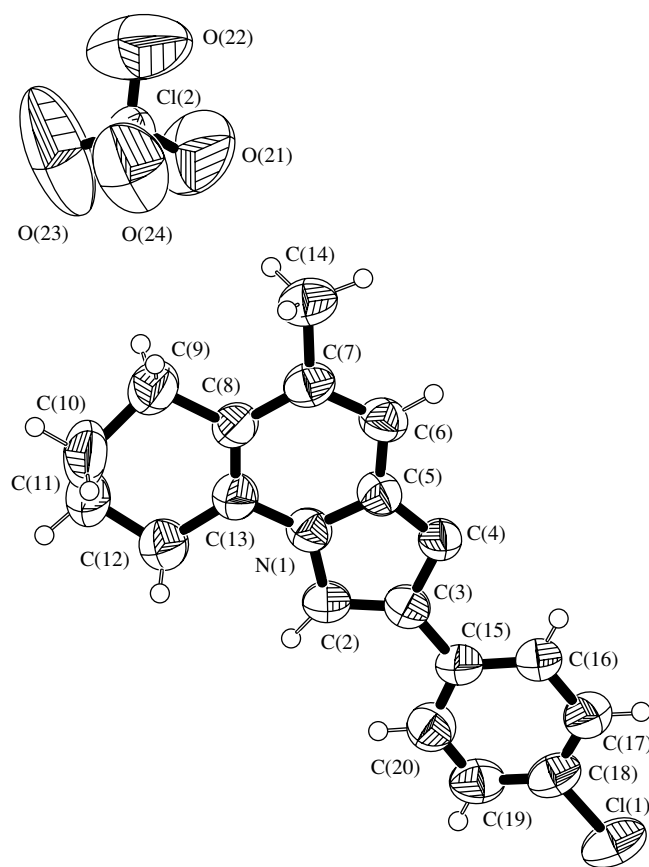

Fig. 4. Molecular structure and atomic numbering for compound **V**.

the C(7) and C(8) atoms are characterized by strong anisotropy, which results in a significant shortening of the distance between these atoms (1.35 Å) with respect to the C(5)–C(6), C(6)–C(7), C(8)–C(9), and C(9)–C(10) distances (Table 2). However, with due regard for the anisotropy of thermal parameters [22], this distance is 1.58 Å, which corresponds to the C(sp^3)–C(sp^3) bond length. In the heterocyclic bicycle of **II**, the single bonds shortened and the double bonds slightly elongated compared to the initial compound **I** [11], which is

in accord with the expected aromatic structure of the pyridine fragment (Scheme 1).

In molecule **III** (Fig. 2), the N(1)···C(10) six-membered ring is planar within 0.01 Å. The O(1), C(1), C(6), C(9), and C(11) atoms lie in the plane of this ring. The C(7) and C(8) atoms deviate from this plane by −0.237 and 0.405 Å, respectively. As in molecule **II**, the ellipsoids of thermal vibrations of the C(7) and C(8) atoms exhibit strong anisotropy and, as a consequence, the distance between these atoms (1.44 Å) is shorter than the C(5)–C(6), C(6)–C(7), C(8)–C(9), and C(9)–
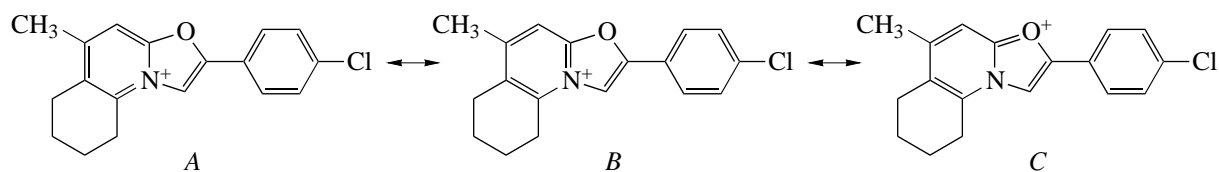
Scheme 2.

C(10) distances (Table 4). However, with due regard for the anisotropy of thermal parameters [22], the C(7)–C(8) distance is 1.57 Å, which corresponds to the C(sp^3)–C(sp^3) bond length. As in the previous case, the structure of the pyridine fragment of the bicycle agrees with the expected aromatic structure (Scheme 1).

In crystals **IV** (Fig. 3), the incomplete occupancy of the positions of the CH$_3$CN solvate molecules led to problems in the course of structure refinement. For their solution, the lengths of the corresponding pairs of bonds in two crystallographically independent molecules were averaged. The N(1)···C(10) six-membered ring is planar within 0.02 Å. The O(1), C(1), C(6), C(9), and C(12) atoms lie in the plane of this ring. The C(7), C(8), and C(11) atoms deviate from this plane by –0.256, 0.340, and –0.204 Å, respectively. The alternation of single and double bonds in the heterocycle corresponds to a nonaromatic pyridone structure (Scheme 1). As in structures **I**–**III**, the distance between the C(7) and C(8) atoms is short (1.44 Å, Table 6). However, after the correction for anisotropy of thermal vibrations was introduced [22], this distance was found to be 1.54 Å. The C(14)···C(19) phenyl ring is planar within 0.013 Å. The Cl(1), C(13), and C(12) atoms lie in the plane of this ring. The O(13) and N(1) atoms deviate from this plane by –0.116 and –0.373 Å, respectively. The dihedral angle between the planes of the pyridone fragment and the aryl group is 86.45°. The structure of two CH$_3$CN solvent molecules is standard and needs no comments.

In cation **V** (Fig. 4), the N(1)···C(13) nine-membered oxazolopyridinium bicycle is planar within 0.03 Å. The C(12), C(14), C(15), C(19), and C(20) atoms lie in the plane of this ring. The C(9), C(10), C(11), C(16), C(17), and C(18) atoms deviate from this plane by 0.119, 0.562, –0.225, 0.275, 0.348, and 0.226 Å, respectively. The C(15)···C(20) phenyl ring is planar within 0.01 Å. The Cl(1) and C(3) atoms lie in the plane of this ring. The structure of the phenyl ring corresponds to the expected aromatic structure. The dihedral angle between the planes of the heterocycle and the phenyl ring is only 7.37°, which indicates the conjugation of the aromatic rings.

The structure of the oxazolopyridinium cation can be represented by three resonance forms; in two of them, the positive charge is localized at the nitrogen atom, and, in the third form, the positive charge is localized at the oxygen atom (see Scheme 2).

The question arises as to which of these formulas represents the structure of the cation more adequately. The C(6)–C(7), C(7)–C(8), and C(8)–C(13) bond lengths (Fig. 5) are equal to 1.378(5), 1.423(5), and 1.359(5) Å, respectively (Table 8). This location of double bonds in the pyridine fragment of the molecule suggests that structure *A* makes a minor contribution. For the final decision between structures *B* and *C*, we searched in the Cambridge Structural Database (Version 11.02) [14] for compounds that contain an amide

group protonated at the oxygen or nitrogen atom (or alkylated at the oxygen atom). As a result, we found that the C=O bond length in these fragments falls in the range 1.25–1.30 Å. Sixty formulas are drawn with a positive charge at the oxygen atom, and more than 200 formulas have a charge at the nitrogen atom. In

Table 8. Bond lengths d (Å) in structure **V**

Bond	d	Bond	d
Cl(1)–C(18)	1.727(4)	C(7)–C(8)	1.423(5)
Cl(2)–O(23)	1.334(4)	C(7)–C(14)	1.506(5)
Cl(2)–O(21)	1.357(4)	C(8)–C(13)	1.359(5)
Cl(2)–O(24)	1.367(4)	C(8)–C(9)	1.515(5)
Cl(2)–O(22)	1.392(5)	C(9)–C(10)	1.555(6)
N(1)–C(5)	1.339(4)	C(10)–C(11)	1.467(7)
N(1)–C(13)	1.381(4)	C(11)–C(12)	1.520(6)
N(1)–C(2)	1.398(4)	C(12)–C(13)	1.501(5)
C(2)–C(3)	1.335(5)	C(15)–C(20)	1.382(5)
C(3)–O(4)	1.394(4)	C(15)–C(16)	1.388(5)
C(3)–C(15)	1.450(5)	C(16)–C(17)	1.376(5)
O(4)–C(5)	1.339(4)	C(17)–C(18)	1.387(6)
C(5)–C(6)	1.374(5)	C(18)–C(19)	1.380(6)
C(6)–C(7)	1.378(5)	C(19)–C(20)	1.370(5)

Table 9. Bond angles ω (deg) in structure **V**

Angle	ω	Angle	ω
O(23)–Cl(2)–O(21)	112.7(5)	C(13)–C(8)–C(7)	120.6(3)
O(23)–Cl(2)–O(24)	108.3(3)	C(13)–C(8)–C(9)	119.0(3)
O(21)–Cl(2)–O(24)	120.1(4)	C(7)–C(8)–C(9)	120.3(3)
O(23)–Cl(2)–O(22)	107.1(6)	C(8)–C(9)–C(10)	110.5(3)
O(21)–Cl(2)–O(22)	100.0(4)	C(11)–C(10)–C(9)	112.9(4)
O(24)–Cl(2)–O(22)	107.5(4)	C(10)–C(11)–C(12)	109.8(4)
C(5)–N(1)–C(13)	121.2(3)	C(13)–C(12)–C(11)	111.8(4)
C(5)–N(1)–C(2)	108.2(3)	C(8)–C(13)–N(1)	118.0(3)
C(13)–N(1)–C(2)	130.5(3)	C(8)–C(13)–C(12)	126.6(3)
C(3)–C(2)–N(1)	106.5(3)	N(1)–C(13)–C(12)	115.4(3)
C(2)–C(3)–O(4)	109.0(3)	C(20)–C(15)–C(16)	118.7(3)
C(2)–C(3)–C(15)	133.5(3)	C(20)–C(15)–C(3)	119.8(3)
O(4)–C(3)–C(15)	117.5(3)	C(16)–C(15)–C(3)	121.6(3)
C(5)–O(4)–C(3)	106.9(2)	C(17)–C(16)–C(15)	121.5(3)
N(1)–C(5)–O(4)	109.4(3)	C(16)–C(17)–C(18)	118.3(4)
N(1)–C(5)–C(6)	123.1(3)	C(19)–C(18)–C(17)	121.1(3)
O(4)–C(5)–C(6)	127.4(3)	C(19)–C(18)–Cl(1)	119.7(3)
C(5)–C(6)–C(7)	116.9(3)	C(17)–C(18)–Cl(1)	119.1(3)
C(6)–C(7)–C(8)	120.1(3)	C(20)–C(19)–C(18)	119.3(4)
C(6)–C(7)–C(14)	120.2(3)	C(19)–C(20)–C(15)	121.0(4)
C(8)–C(7)–C(14)	119.8(3)		

pyridones, the C=O bond lengths fall in the range between 1.21 and 1.25 Å, which indicates that protonation (or alkylation) of the oxygen heteroatom results in an elongation of the double carbon–oxygen bond. In structure **V**, the C(5)–O(4) bond length is 1.339(4) Å. This value is intermediate between the single and double C–O bond lengths in the positively charged amide group. The N(1)–C(5) bond length is also 1.339(4) Å. This bond is shorter than the two other C–N bonds at the same nitrogen atom [1.381(4) and 1.398(4) Å]. Based on these arguments, we concluded that the structure of the oxazolopyridinium cation can be described by a superposition of the *B* and *C* formulas (with a slightly larger contribution of the *B* structure). Probably, the structure of the cation is most adequately represented by the following charge delocalization:
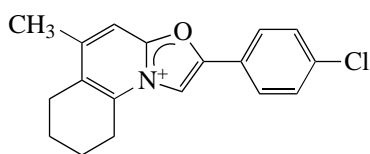
Scheme 3.

The thermal ellipsoids of the oxygen atoms in the perchlorate anion exhibit strong anisotropy in the plane perpendicular to the Cl–O bond (Fig. 4). This suggests some degree of rotational freedom of the perchlorate ion about the chlorine atom.

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