

STRUCTURE
OF ORGANIC COMPOUNDS

X-ray Mapping in Heterocyclic Design:
X. X-ray Diffraction Study
of 4-Methyl-6,7,8,9-Tetrahydro-2-Quinolone

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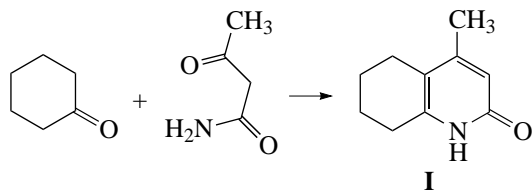
Abstract—The structure of 4-methyl-6,7,8,9-tetrahydro-2-quinolone is studied by the single-crystal X-ray diffraction technique ($a = 6.6890(17)$ Å, $b = 7.926(2)$ Å, $c = 8.993(3)$ Å, $\alpha = 85.50(2)^\circ$, $\beta = 68.22(2)^\circ$, $\gamma = 82.89(2)^\circ$, $Z = 2$, and space group $P\bar{1}$). The structure is solved by direct methods and refined to $R_1 = 0.0592$ and $wR_2 = 0.1206$. In the crystal, intermolecular hydrogen bonds link molecules into centrosymmetric dimers. © 2003 MAIK "Nauka/Interperiodica".

INTRODUCTION

This work continues our structural investigations of the heterocyclic compounds that are able to undergo various rearrangements, in particular, cyclization reactions [1–10]. As in our previous papers, we step-by-step perform the X-ray diffraction studies of all the intermediates and final products of multistage cyclization reactions and rearrangements. Substituted pyridones are interesting objects for these investigations, because they are characterized by a high reactivity. In this study, we determined the structure of 4-methyl-6,7,8,9-tetrahydro-2-quinolone. At present, data on its molecular and crystal structures are not available in the Cambridge Structural Database (Version 04.02) [11].

EXPERIMENTAL

4-Methyl-6,7,8,9-tetrahydro-2-quinolone (**I**) was synthesized according to the procedure described in [12]:



The ^1H NMR spectrum was recorded on a Bruker AM-360 spectrometer (field strength, 8.46 T; operating frequency, 360.14 MHz for protons; DMSO- d_6 ; internal standard, TMS). Based on the available data, the NMR signals were assigned as follows (δ , ppm): 11.50 (s) H(1); 5.90 (s) H(3); 2.48 (t) H(9A), H(9B); 2.34 (t) H(6A), H(6B); 2.03 (s) H(1A), H(1B), H(1C); 1.72 (m) H(7A), H(7B), H(8A), H(8B).

The intensities of diffraction reflections were measured on a CAD4 diffractometer [13] ($\text{MoK}\alpha$ radiation,

graphite monochromator, ω scan mode) at room temperature. The unit cell parameters were determined and refined using 25 reflections in the θ range 13° – 15° . Selected experimental parameters and crystal data are included in Table 1.

Since the crystals of the compound studied are small in size and have small linear absorption coefficients, the data were not corrected for absorption. The primary

Table 1. Crystal data and details of the X-ray diffraction experiment and refinement of structure **I**

Compound	$\text{C}_{10}\text{H}_{13}\text{NO}$
Molecular weight	163.21
Crystal system	Triclinic
Space group	$P\bar{1}$
a , Å	6.6890(17)
b , Å	7.926(2)
c , Å	8.993(3)
α , deg	85.50(2)
β , deg	68.22(2)
γ , deg	82.89(2)
V , Å ³	439.1(2)
Z	2
ρ_{calc} , g/cm ³	1.235
$\mu(\text{MoK}\alpha)$, cm ⁻¹	0.080
Crystal size, mm	0.30 × 0.30 × 0.30
θ_{max} , deg	26
Number of reflections with $I \geq 2\sigma(I)$ /number of parameters	1618/162
R_1/wR_2	0.0592/0.1206
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e/Å ³	0.203/−0.141

Table 2. Bond lengths d (Å) for non-hydrogen atoms in structure **I**

Bond	d
N(1)–C(2)	1.3541(16)
N(1)–C(10)	1.3830(18)
C(2)–O(2)	1.2578(17)
C(2)–C(3)	1.4107(18)
C(3)–C(4)	1.374(2)
C(4)–C(5)	1.4172(18)
C(4)–C(11)	1.5122(18)
C(5)–C(10)	1.3541(17)
C(5)–C(6)	1.514(2)
C(6)–C(7)	1.503(2)
C(7)–C(8)	1.451(2)
C(8)–C(9)	1.509(2)
C(9)–C(10)	1.4754(18)

Table 3. Bond angles ω (deg) for non-hydrogen atoms in structure **I**

Angle	ω
C(2)–N(1)–C(10)	125.10(10)
O(2)–C(2)–N(1)	120.04(11)
O(2)–C(2)–C(3)	124.34(12)
N(1)–C(2)–C(3)	115.61(13)
C(4)–C(3)–C(2)	121.00(12)
C(3)–C(4)–C(5)	120.58(11)
C(3)–C(4)–C(11)	118.99(12)
C(5)–C(4)–C(11)	120.43(13)
C(10)–C(5)–C(4)	118.52(13)
C(10)–C(5)–C(6)	119.81(11)
C(4)–C(5)–C(6)	121.65(11)
C(7)–C(6)–C(5)	113.50(12)
C(8)–C(7)–C(6)	114.38(16)
C(7)–C(8)–C(9)	112.60(13)
C(10)–C(9)–C(8)	111.96(12)
C(5)–C(10)–N(1)	119.14(11)
C(5)–C(10)–C(9)	125.08(13)
N(1)–C(10)–C(9)	115.78(11)

Table 4. Parameters of interatomic contacts in structure **I**

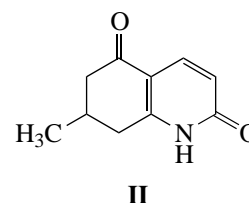
D–H	$d(D-H)$	$d(D\cdots A)$	$d(H\cdots A)$	ωDHA	A	Symmetry operation
N(1)–H(1)	0.82(1)	2.772(1)	1.96(1)	174(1)	O(2)	(2– x ; 1– y ; 1– z)
C(7)–H(7A)	1.07(2)	3.515(2)	2.66(2)	137(1)	O(2)	(1– x ; 1– y ; 1– z)
C(8)–H(8B)	0.99(2)	3.536(2)	2.58(2)	163(1)	O(2)	(x ; y ; $z-1$)
C(11)–H(11C)	0.89(2)	3.547(2)	2.81(2)	141(2)	O(2)	($x-1$; y ; z)

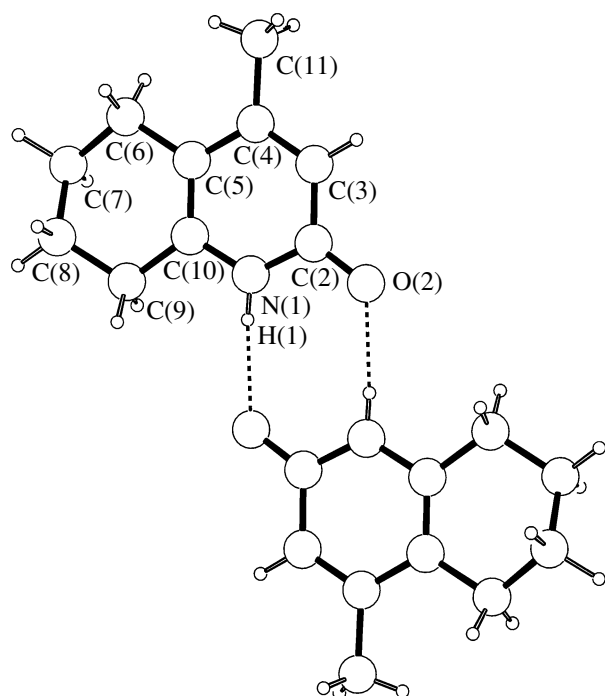
Note: D is a donor, A is an acceptor, and H is a hydrogen atom; the d distances and ω angles are given in angstroms and degrees, respectively.

processing of the experimental data was performed with the WinGX98 program package [14], and all further calculations were performed with the SHELX97 program package [15]. The crystal structure was solved by direct methods. The positional and thermal parameters were refined in the anisotropic approximation for all the non-hydrogen atoms. The hydrogen atoms were located from the difference Fourier synthesis and refined in the isotropic approximation. The interatomic distances and bond angles are listed in Tables 2 and 3, respectively. The parameters of the interatomic contacts involving the hydrogen atoms are given in Table 4. The crystal data for compound **I** are deposited in the Cambridge Structural Database (deposit no. 198666). The molecular structure of **I** and the atomic numbering are shown in the figure, which was drawn with the use of the PLUTON96 program [16].

RESULTS AND DISCUSSION

In molecule **I**, the N(1)C(2)C(3)C(4)C(5)C(10) six-membered ring is planar within 0.014 Å. The O(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 –0.236 and 0.425 Å, respectively. In crystal **I**, intermolecular hydrogen bonds link molecules into centrosymmetric dimers (figure, Table 4). In the Cambridge Structural Database (Version 04.02) [11], we found a compound with a similar structure, namely, 7,8-dihydro-7-methyl-2,5(1*H*,6*H*)-quinoline-2,5-dione (**II**) [17]





Molecular structure with the atomic numbering and formation of the centrosymmetric dimer in structure **I**.

In both structures, the ellipsoids of thermal vibrations of the C(7) and C(8) atoms (the numberings are identical; see figure) are elongated almost perpendicular to the plane of the heterocyclic system. As a consequence, the distance between the C(7) and C(8) atoms is significantly shorter [1.451(2) Å] than the C(5)–C(6), C(6)–C(7), C(8)–C(9), and C(9)–C(10) distances (Table 2). However, with allowance made for strong anisotropy of the thermal parameters [18], the C(7)–C(8) distance is 1.58 Å, which is consistent with the sp^3 hybridization. The structure of the heterocyclic fragment of the bicycle in molecules **I** and **II** corresponds to the pyridone, rather than pyridol, tautomer.

The fusion of the cyclohexene and pyridone fragments in molecule **I** along the C(5)–C(10) double bond results in a slight shortening of this bond (1.354 Å) in comparison with the other double bond, namely, C(3)–C(4) (1.374 Å); that is, the carbocyclic fragment slightly contracts the bond in the adjacent heterocycle. Note that the environment of the C(5)–C(10) double bond in the bicycle includes the C(4), C(6), C(9), and N(1) atoms and has an asymmetric configuration: the C(6)–C(5)–C(4) exocyclic angle is 121.7°, whereas the C(9)–C(10)–N(1) angle is only 115.8°. This leads to a close spacing between the C(9)H₂ methylene fragment and the nitrogen atom, which should be considered in the analysis of the reactivity of molecule **I**. For example, in the alkylation reactions, the N(1) nitrogen atom can be considerably shielded by the C(9) methylene link.

In the coming months, we are going to study the reactivity of compound **I** and to perform X-ray structure analysis of the products obtained.

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