

STRUCTURE
OF ORGANIC COMPOUNDS

X-ray Mapping in Heterocyclic Design:
16. X-ray Diffraction Study of 1-(4-Chlorophenacyl)-4-Methyl-
1,5,6,7-Tetrahydro-2H-Cyclopenta[*b*]pyridin-2-one

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Abstract—The structure of 1-(4-chlorophenacyl)-4-methyl-1,5,6,7-tetrahydro-2H-cyclopenta[*b*]pyridin-2-one is studied using single-crystal X-ray diffraction. The structure ($a = 37.006(8)$ Å, $b = 8.967(3)$ Å, $c = 27.911(3)$ Å, $\beta = 96.52(2)^\circ$, $Z = 24$, space group $P2_1/c$) is solved by direct methods and refined to $R_1 = 0.0608$ and $wR_2 = 0.1170$. Six crystallographically independent molecules differ in the dihedral angle between the phenyl and heterocycle planes. The formation of Cl...Cl aggregates is discussed. © 2005 Pleiades Publishing, Inc.

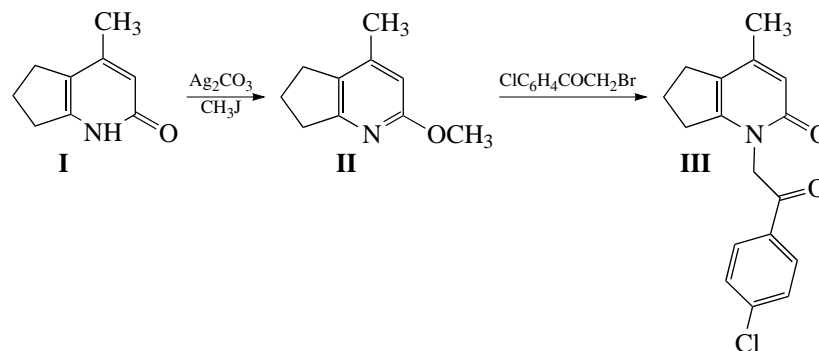
INTRODUCTION

This study continues a series of structural investigations of heterocyclic compounds that are able to undergo different transformations, including cyclization reactions [1–10]. As was done in our previous works, we perform the step-by-step structure determination of all the intermediates and final products of multistage cyclization reactions and rearrangements. In particular, substituted pyridones are characterized by a high reactivity and, therefore, serve as objects of interest in our investigations. In this work, we determined the structure of 1-(4-chlorophenacyl)-4-methyl-1,5,6,7-

tetrahydro-2H-cyclopenta[*b*]pyridin-2-one. Data on the molecular and crystal structure of this compound are not available in the Cambridge Structural Database (version 11.03) [11].

EXPERIMENTAL TECHNIQUE

The initial compound **I** was prepared and studied earlier in [2]. 1-(4-Chlorophenacyl)-4-methyl-1,5,6,7-tetrahydro-2H-cyclopenta[*b*]pyridin-2-one (**III**) was synthesized according to the procedure developed earlier in [3]:



The intermediate product **II** was a liquid. Its structure was confirmed by ^1H NMR spectroscopy. The ^1H NMR spectra were recorded on a Bruker AM-360 spectrometer (field strength, 8.46 T; operating frequency, 360.14 MHz for protons; $\text{DMSO}-d_6$; internal standard, TMS). The signals in the NMR spectra were assigned taking into account the data available in the literature. The atomic numbering in both compounds corresponds

to that used in Fig. 1 (see below). For compound **II** (δ , ppm): 2.12 [m, 2H, C(7)H₂], 2.27 [s, 3H, C(10)H₃], 2.67 [t, 2H, C(6)H₂], 2.86 [t, 2H, C(8)H₂], 3.65 [s, 3H, OCH₃], 6.09 [s, 1H, C(3)H]. For compound **III** (δ , ppm): 2.10 [m, 2H, C(7)H₂], 2.15 [s, 3H, C(10)H₃], 2.75 [m, 4H, C(6)H₂ + C(8)H₂], 5.34 [s, 2H, C(11)H₂], 6.03 [s, 1H, C(3)H], 7.55, 8.07 (dd, 4H, Ar).

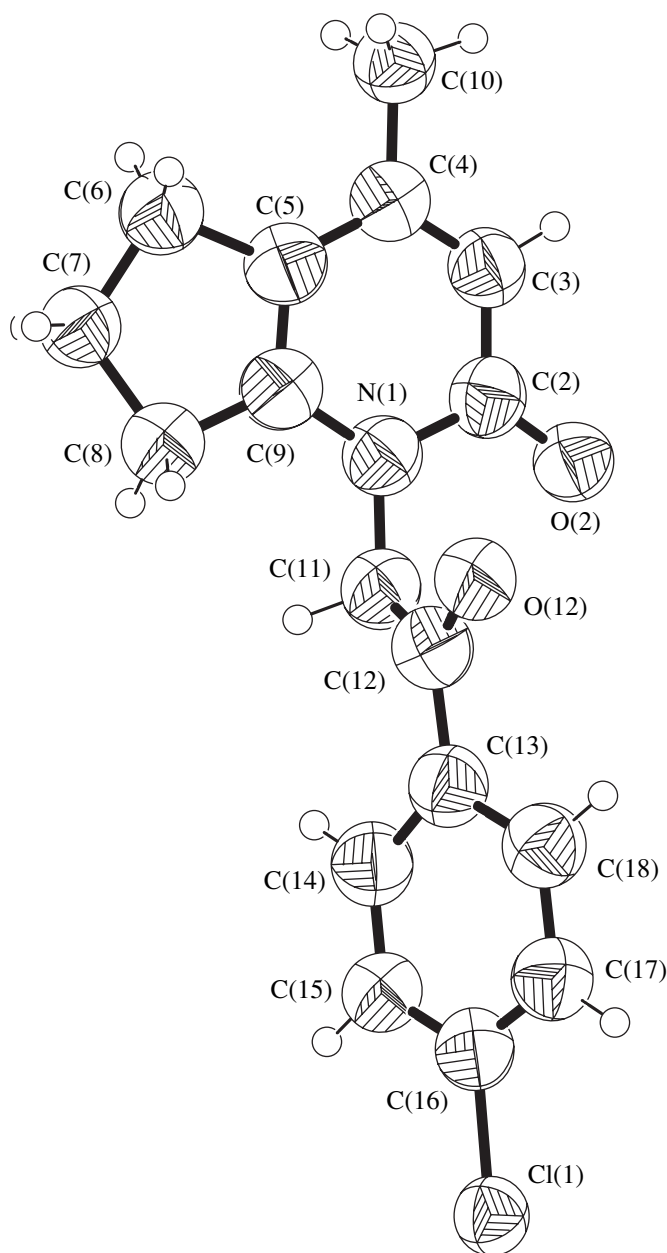


Fig. 1. Molecular structure and atomic numbering for compound **III**.

The experimental intensities of diffraction reflections were obtained for compound **III** on a CAD4 diffractometer [12] ($\text{CuK}\alpha$ radiation, graphite monochromator, ω scan mode) at room temperature. The unit cell parameters were determined and refined using 25 reflections in the θ range 22° – 25° . The main experimental parameters and crystal data for compound **III** are summarized in Table 1. No absorption correction was introduced because of the small linear absorption coefficient of the compound under investigation and the small sizes of its crystals. The primary processing of the experimental data set was performed with the

Table 1. Main crystal data, details of the X-ray diffraction experiment, and refinement parameters for the structure of compound **III**

Empirical formula	$\text{C}_{17}\text{H}_{16}\text{NO}_2\text{Cl}$
M	301.76
Crystal system	Monoclinic
Space group, Z	$P2_1/c$, 24
a , Å	37.006(8)
b , Å	8.967(3)
c , Å	27.911(5)
β , deg	96.52(2)
V , Å ³	9202(4)
ρ_{calcd} , g/cm ³	1.307
$\mu(K\alpha)$, mm ⁻¹	2.333
θ range, deg	1.20–69.99
h, k, l index range	$-44 \leq h \leq 45, 0 \leq k \leq 10, 0 \leq l \leq 34$
Crystal size, mm	$0.22 \times 0.20 \times 0.18$
Number of reflections measured	17437
Number of unique reflections	17437
Number of reflections with $I \geq 2\sigma(I)$	15846
Number of reflections in the refinement/Number of parameters refined	17437/1142
S	1.408
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0608/0.1170
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e/Å ³	0.384/–0.332

WinGX98 program package [13]. All the subsequent calculations were carried out with the SHELX97 program package [14]. The crystal structure was solved by direct methods. All the non-hydrogen atoms were refined in the anisotropic approximation. The hydrogen atoms were introduced into the calculated positions and refined in the isotropic approximation. The linear molecular parameters were averaged over all the crystallographically independent molecules; therefore, only one set of interatomic distances and angles is given in Tables 2 and 3, respectively. The crystal data for compound **III** have been deposited with the Cambridge Structural Database (deposition no. 268723). The molecular structure of compound **III** with the atoms depicted as thermal ellipsoids and the atomic numbering are shown in Fig. 1, which was drawn using the ORTEP program [15]. The arrangement of molecules in the asymmetric part of the unit cell is given in Fig. 2, which was obtained with the PLUTON96 program [16].

RESULTS AND DISCUSSION

Crystals of compound **III** contain six crystallographically independent molecules *A*–*F* (Fig. 2). These molecules differ in the dihedral angles between the

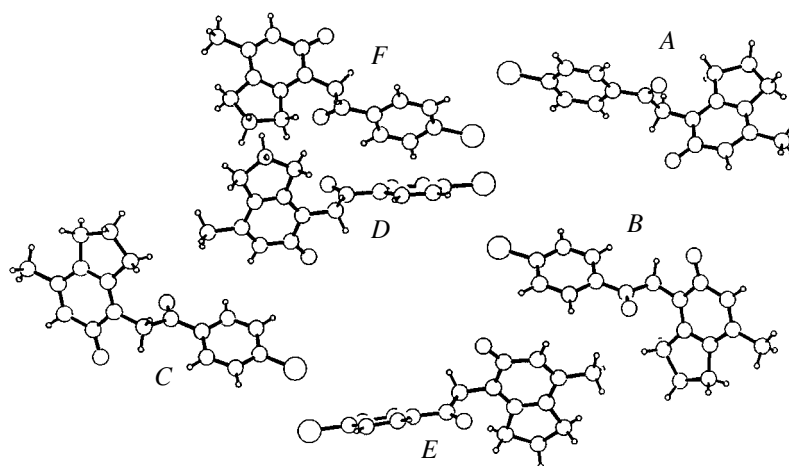


Fig. 2. Spatial arrangement of crystallographically independent molecules of compound **III**.

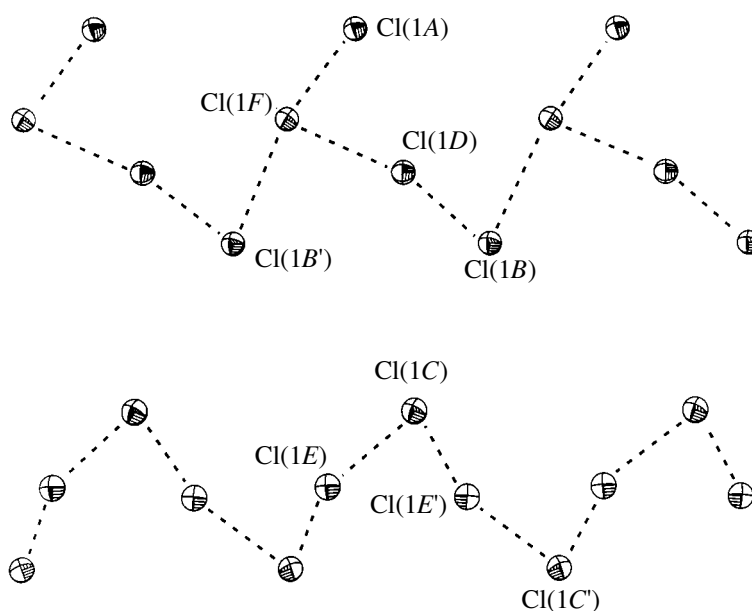


Fig. 3. Structure of *Hal* aggregates in the crystal of compound **III**.

phenyl and heterocycle planes. The dihedral angles are equal to $88.05(4)^\circ$, $66.58(4)^\circ$, $65.72(4)^\circ$, $62.21(5)^\circ$, $58.79(5)^\circ$, and $80.39(4)^\circ$, respectively. The large number of independent molecules evoked our interest in the packing. We found that the Cl atoms are located close to one another (Fig. 3). Such contacts have been described in the literature [17–20], and the formation of similar *Hal* aggregates in the compounds with a low halogen content has been explained by the chlorophobic interaction [19]. The Cl...Cl distances in these aggregates amount to 4.3 \AA [20]. In compound **III**, the Cl(1A), Cl(1F), Cl(1D), and Cl(1B) atoms form a cluster chain in which the distances between the neighbor-

ing atoms are equal to $3.889(2)$, $4.350(2)$, and $3.962(2) \text{ \AA}$, respectively. The Cl(1A)...Cl(1F)...Cl(1D) and Cl(1F)...Cl(1D)...Cl(1B) angles are $64.17(8)^\circ$ and $140.02(9)^\circ$, respectively. The shortest Cl(1F)...Cl(1B') distance between the clusters is significantly larger and equal to $5.151(2) \text{ \AA}$. The Cl(1C) and Cl(1E) atoms, together with their symmetrically equivalent atoms Cl(1C') and Cl(1E'), form a zigzag chain along the twofold screw axis. The Cl(1E)...Cl(1C) and Cl(1C)...Cl(1E') distances are equal to $4.125(2)$ and $3.943(2) \text{ \AA}$, respectively; and the Cl(1E)...Cl(1C)...Cl(1E') and Cl(1C)...Cl(1E')...Cl(1C') angles are $68.91(7)^\circ$ and $156.12(9)^\circ$, respectively.

Table 2. Average bond lengths d (Å) in structure of compound **III**

Bond	d	Bond	d
C1(1)–C(16)	1.7435(8)	C(7)–C(8)	1.5408(10)
N(1)–C(9)	1.3631(9)	C(8)–C(9)	1.4734(10)
N(1)–C(2)	1.4178(9)	C(11)–C(12)	1.5188(10)
N(1)–C(11)	1.4510(9)	C(12)–O(12)	1.2273(9)
C(2)–O(2)	1.2484(9)	C(12)–C(13)	1.4758(9)
C(2)–C(3)	1.4207(9)	C(13)–C(14)	1.3878(10)
C(3)–C(4)	1.3498(10)	C(13)–C(18)	1.4077(10)
C(4)–C(5)	1.3924(10)	C(14)–C(15)	1.3760(10)
C(4)–C(10)	1.5095(10)	C(15)–C(16)	1.3496(10)
C(5)–C(9)	1.3456(9)	C(16)–C(17)	1.3696(10)
C(5)–C(6)	1.5071(10)	C(17)–C(18)	1.3794(10)
C(6)–C(7)	1.4904(10)		

Table 3. Selected bond angles ω (deg) in molecule **III**

Angle	ω	Angle	ω
C(9)–N(1)–C(2)	121.78(7)	C(5)–C(9)–C(8)	115.03(7)
C(9)–N(1)–C(11)	121.43(7)	N(1)–C(9)–C(8)	124.42(7)
C(2)–N(1)–C(11)	116.36(7)	N(1)–C(11)–C(12)	112.13(7)
O(2)–C(2)–N(1)	118.88(7)	O(12)–C(12)–C(13)	120.25(7)
O(2)–C(2)–C(3)	126.76(8)	O(12)–C(12)–C(11)	120.57(7)
N(1)–C(2)–C(3)	114.23(7)	C(13)–C(12)–C(11)	118.85(7)
C(4)–C(3)–C(2)	124.05(8)	C(14)–C(13)–C(18)	116.64(7)
C(3)–C(4)–C(5)	117.77(7)	C(14)–C(13)–C(12)	120.83(7)
C(3)–C(4)–C(10)	120.45(8)	C(18)–C(13)–C(12)	122.46(7)
C(5)–C(4)–C(10)	121.49(8)	C(15)–C(14)–C(13)	122.02(8)
C(9)–C(5)–C(4)	121.24(7)	C(16)–C(15)–C(14)	119.54(8)
C(9)–C(5)–C(6)	109.42(7)	C(15)–C(16)–C(17)	121.11(8)
C(4)–C(5)–C(6)	129.16(7)	C(15)–C(16)–Cl(1)	119.65(7)
C(7)–C(6)–C(5)	104.61(6)	C(17)–C(16)–Cl(1)	118.98(6)
C(6)–C(7)–C(8)	109.25(7)	C(16)–C(17)–C(18)	119.75(8)
C(9)–C(8)–C(7)	101.64(6)	C(17)–C(18)–C(13)	120.77(8)
C(5)–C(9)–N(1)	120.54(7)		

In all the molecules, the N(1)–C(9) six-membered ring is planar within 0.036 Å. In molecules *A*, *C*, and *D*, the O(2), C(6), C(7), C(8), C(10), and C(11) atoms lie in the plane of this ring. In molecule *B*, the C(6) atom deviates from the plane by 0.120(2) Å. In molecules *E* and *F*, the C(7) atom deviates by 0.129(3) and 0.200(2) Å, respectively. It is interesting to note that the cyclopentene fragments are actually planar, as is the case in the crystal of compound **I** [2].

Our further studies will concentrate on the reactivity of compound **III** and the X-ray structure analysis of the products obtained.

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