

STRUCTURE
OF ORGANIC COMPOUNDS

X-ray Mapping in Heterocyclic Design: XII. X-ray Diffraction Study of 2-Pyridones Containing Cycloalkane Fragments Annulated to the C(5)–C(6) Bond

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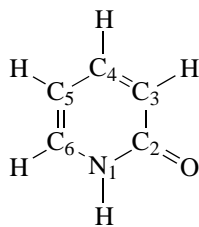
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Abstract—The structures of 4,6-dimethyl-1*H*-pyridin-2-one [$a = 6.125(2)$ Å, $b = 15.153(4)$ Å, and $c = 14.477(4)$ Å, $Z = 8$, space group $Pbca$], the 2 : 1 : 1 complex of 4-methyl-1,5,6,7-tetrahydro-2*H*-cyclopenta[*b*]pyridin-2-one with phosphoric acid and methanol [$a = 11.181(2)$ Å, $b = 14.059(6)$ Å, $c = 13.593(4)$ Å, $\beta = 97.78(2)^\circ$, $Z = 8$, space group $P2_1/n$], 4-methyl-1,5,6,7,8,9-hexahydro-2*H*-cyclohepta[*b*]pyridin-2-one [$a = 12.565(6)$ Å, $b = 5.836(6)$ Å, $c = 13.007(3)$ Å, $\beta = 93.10(3)^\circ$, $Z = 4$, space group $P2_1/n$], and 4-methyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridin-2(1*H*)-one [$a = 12.955(3)$ Å, $b = 6.1595(15)$ Å, $c = 13.038(3)$ Å, $\beta = 95.50(2)^\circ$, $Z = 4$, space group $P2_1/n$] are determined by single-crystal X-ray diffraction. The structures are solved by direct methods and refined by the full-matrix least-squares procedure in the anisotropic approximation to $R = 0.0755$, 0.0644 , 0.0754 , and 0.0569 , respectively. The structures of 4-methyl-1,5,6,7-tetrahydro-2*H*-cyclopenta[*b*]pyridin-2-one [$a = 7.353(4)$ Å, $b = 8.176(4)$ Å, $c = 13.00(1)$ Å, $\beta = 105.64(2)^\circ$, $Z = 4$, space group $P2_1/c$] and 2-oxo-1,2,5,6,7,8-hexahydroquinoline-3-carbonitrile [$a = 5.9870(2)$ Å, $b = 16.5280(5)$ Å, $c = 9.6540(3)$ Å, $\beta = 111.52(4)^\circ$, $Z = 4$, space group $P2_1/c$] are studied by the powder diffraction technique. The structures are solved using the grid search procedure and refined by the Rietveld method to $R_{wp} = 0.108$ and 0.058 , $R_{exp} = 0.032$ and 0.027 , $R_p = 0.076$ and 0.043 , $R_b = 0.123$ and 0.077 , and $\chi^2 = 7.9$ and 3.64 , respectively. In all the structures, hydrogen bonds involving the N, H, and O atoms of the pyridone fragment are formed. © 2004 MAIK “Nauka/Interperiodica”.

INTRODUCTION

This study continues our investigation into the structure of heterocyclic compounds that are able to undergo various rearrangements and, in particular, to enter into cyclization reactions [1–12]. As was done in our previous works, we perform an 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 (scheme 1).

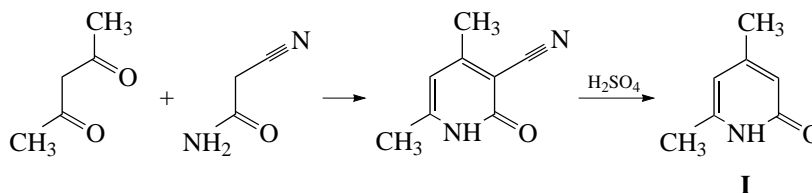


Scheme 1

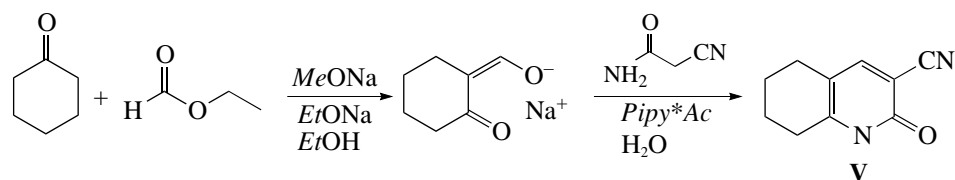
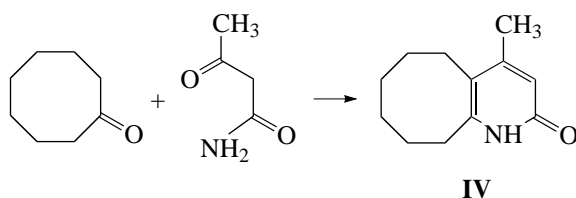
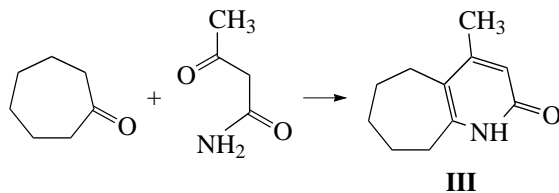
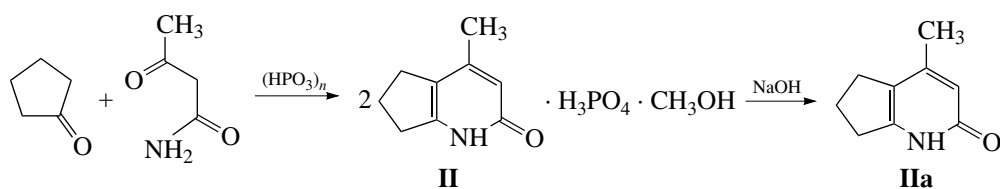
In this paper, we report the structures of 4,6-dimethyl-1*H*-pyridin-2-one (**I**) and a number of its analogues that contain cycloalkane fragments annulated to the C(5)–C(6) bond, namely, 4-methyl-1,5,6,7-tetrahydro-2*H*-cyclopenta[*b*]pyridin-2-one (**IIa**), its 2 : 1 : 1 complex with phosphoric acid and methanol (**II**), 4-methyl-1,5,6,7,8,9-hexahydro-2*H*-cyclohepta[*b*]pyridin-2-one (**III**), 4-methyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridin-2(1*H*)-one (**IV**), and 2-oxo-1,2,5,6,7,8-hexahydroquinoline-3-carbonitrile (**V**). Data on the molecular structures of the compounds discussed in this paper are not available in the Cambridge Structural Database (version 11.02) [13].

EXPERIMENTAL

The synthesis of the compounds was performed according to the following schemes:



Scheme 2



Compound **I** was prepared using the procedure described in [14]. Compounds **II**, **III**, and **IV** were synthesized according to the modified procedure used in [15]: acetoacetamide (16 g), the cycloalkanone (equimolar amount), and polyphosphoric acid (80 g) were gently heated on stirring with a glass rod in a bea-

ker. An exothermic reaction began at about 70°C, and the temperature of the mixture abruptly increased to 140°C. The reaction mixture was then stirred at 100°C to a homogeneous state (for about 5 min) and poured into hot water. A dark solution and liquid resin were formed. The resinoid residue was removed, and the

Table 1. Physicochemical parameters of the compounds synthesized

Compound	Melting temperature T_m , °C	^1H NMR	Reference
I	180–182	6.04 [1H, s, C(5)H]; 5.92 [1H, s, C(3)H]; 2.23 (3H, s, 6-CH ₃); 2.13 (3H, s, 4-CH ₃) (acetone- <i>d</i> ₆)	[14]
IIa	245–248	5.87 [1H, s, C(3)H]; 2.72 [2H, t, C(8)H ₂]; 2.61 [2H, t, C(6)H ₂]; 2.06 [3H, s, C(10)H ₃]; 2.04 [2H, m, C(7)H ₂] (DMSO- <i>d</i> ₆)	[15]
III	258–260	5.88 [1H, s, C(3)H]; 2.62 [2H, t, C(10)H ₂]; 2.48 [2H, t, C(6)H ₂]; 2.08 [3H, s, C(12)H ₃]; 1.78 [2H, m, C(9)H ₂]; 1.54 [4H, m, C(7)H ₂ , C(8)H ₂] (DMSO- <i>d</i> ₆)	[15]
IV	230–233	5.99 [1H, s, C(3)H]; 2.58 (2H, t, C(11)H ₂); 2.46 [2H, t, C(6)H ₂]; 2.09 [3H, s, C(13)H ₃]; 1.59 [2H, m, C(10)H ₂]; 1.51 [2H, m, C(7)H ₂]; 1.34 [4H, m, C(8)H ₂ , C(9)H ₂] (DMSO- <i>d</i> ₆)	–
V	250–257	7.87 [1H, s, C(4)H]; 2.56 [2H, t, C(7)H ₂]; 2.43 [2H, t, C(9)H ₂]; 1.66 (4H, m, C(7)H ₂ , C(8)H ₂) (DMSO- <i>d</i> ₆)	[16]

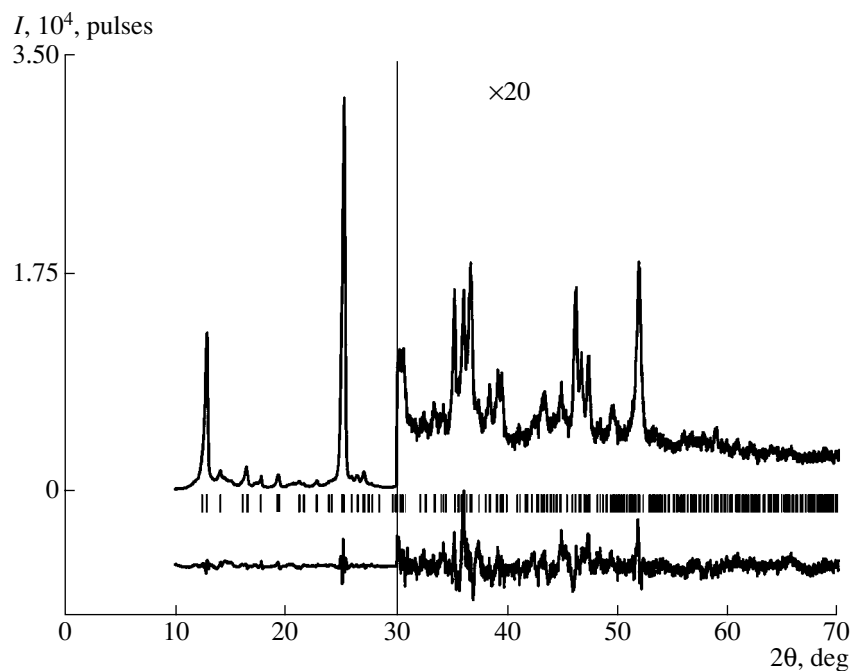


Fig. 1. Experimental and difference (Rietveld refinement) spectra for compound IIa.

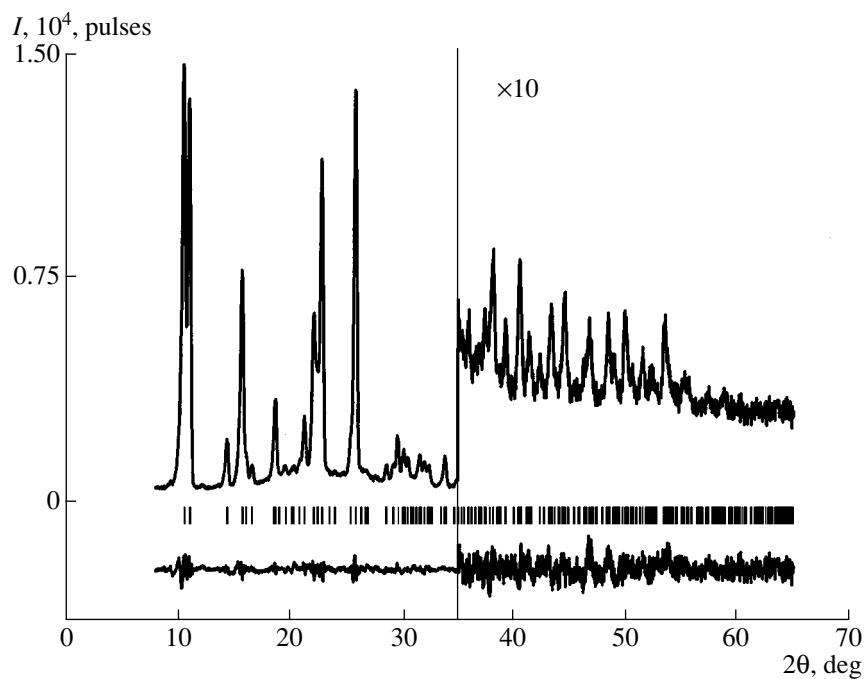


Fig. 2. Experimental and difference (Rietveld refinement) spectra for compound V.

solution was neutralized with solid sodium hydrogen-carbonate until the formation of the precipitate was completed. The precipitate was filtered off and washed with water and acetone. In the case of cyclopentanone, the precipitate contained H_3PO_4 . Recrystallization of

this precipitate resulted in the formation of complex II, which contained methanol and phosphoric acid. Complex II was treated in 10% aqueous solution of NaOH with the formation of compound IIa. The yield of compound IIa was 50%, and the yields of compounds III

Table 2. Crystal data, data collection, and refinement parameters for the structures studied

Empirical formula	C ₇ H ₉ NO (I)	C ₁₉ H ₂₉ N ₂ O ₇ P (II)	C ₉ H ₁₁ NO (IIa)	C ₁₁ H ₁₅ NO (III)	C ₁₂ H ₁₇ NO (IV)	C ₁₀ H ₁₀ N ₂ O (V)
Molecular weight	123.15	428.42	149.19	177.24	191.27	174.20
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> , Å	6.125(2)	11.181(2)	7.353(4)	12.565(6)	12.955(3)	5.9870(2)
<i>b</i> , Å	15.153(4)	14.059(6)	8.176(4)	5.836(6)	6.1595(15)	16.5280(5)
<i>c</i> , Å	14.477(4)	13.593(4)	13.00(1)	13.007(3)	13.038(3)	9.5640(3)
β, deg	90	97.78(2)	105.64(2)	93.10(3)	95.50(2)	111.52(4)
<i>V</i> , Å ³	1343.6(7)	2117.1(12)	752.6(8)	952.5(10)	1035.6(4)	888.71(5)
<i>Z</i>	8	4	4	4	4	4
ρ _{calcd} , g/cm ³	1.218	1.344	1.313	1.236	1.227	1.304
μ, cm ⁻¹	0.82	1.73	0.86	0.79	0.78	0.70
θ range, deg	2.69 – 24.97	2.09 – 25.98	3 – 40	2.20 – 24.97	2.12 – 19.99	3 – 40
Index ranges	0 ≤ <i>h</i> ≤ 7 0 ≤ <i>k</i> ≤ 18 0 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 13 0 ≤ <i>k</i> ≤ 17 0 ≤ <i>l</i> ≤ 16	0 ≤ <i>h</i> ≤ 5 0 ≤ <i>k</i> ≤ 6 -9 ≤ <i>l</i> ≤ 9	-14 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 6 0 ≤ <i>l</i> ≤ 15	-12 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 5 0 ≤ <i>l</i> ≤ 12	-4 ≤ <i>h</i> ≤ 4 0 ≤ <i>k</i> ≤ 7 0 ≤ <i>l</i> ≤ 3
Crystal size, mm	0.32 × 0.35 × 0.41	0.31 × 0.32 × 0.34		0.34 × 0.37 × 0.49	0.28 × 0.30 × 45	
Number of reflections collected	1120	4269		1576	962	
Number of unique reflections	1120	4095		1509	913	
Number of reflections in least-squares refinement/Number of parameters refined	1120/119	4095/379		1509/174	913/132	
<i>Goof</i>	1.105	1.023		0.926	0.941	
<i>R</i> ₁ / <i>wR</i> ₂ for <i>I</i> ≥ 2σ(<i>I</i>)	0.0755/0.1825	0.0644/0.1319		0.0754/0.1343	0.0569/0.1028	
<i>R</i> ₁ / <i>wR</i> ₂ for all reflections	0.1523/0.2209	0.1328/0.1622		0.2563/0.2091	0.1569/0.1404	
Δρ _{max} /Δρ _{min} , e/Å ³	0.222/-0.298	0.209/-0.233		0.212/-0.209	0.201/-0.165	
Scan step			0.02			0.02
<i>R</i> _{wp}			0.108			0.058
<i>R</i> _{exp}			0.032			0.027
<i>R</i> _p			0.076			0.043
<i>R</i> _b			0.123			0.077
χ ²			7.9			3.64

Table 3. Bond lengths d (Å) in structure **I**

Bond	d	Bond	d
N(1)–C(6)	1.3584(8)	C(3)–C(4)	1.3526(9)
N(1)–C(2)	1.3684(8)	C(4)–C(5)	1.3951(9)
N(1)–H(1)	0.874(5)	C(4)–C(8)	1.5215(10)
O(2)–C(2)	1.2534(8)	C(5)–C(6)	1.3519(8)
C(2)–C(3)	1.4227(9)	C(6)–C(7)	1.4983(9)

Table 4. Bond angles ω (deg) in structure **I**

Angle	ω	Angle	ω
C(6)–N(1)–C(2)	124.55(5)	C(3)–C(4)–C(5)	124.55(5)
C(6)–N(1)–H(1)	119.4(3)	C(3)–C(4)–C(8)	119.4(3)
C(2)–N(1)–H(1)	116.0(3)	C(5)–C(4)–C(8)	116.0(3)
O(2)–C(2)–N(1)	119.58(5)	C(6)–C(5)–C(4)	119.58(5)
O(2)–C(2)–C(3)	125.01(6)	C(5)–C(6)–N(1)	125.01(6)
N(1)–C(2)–C(3)	115.40(5)	C(5)–C(6)–C(7)	115.40(5)
C(4)–C(3)–C(2)	121.18(6)	N(1)–C(6)–C(7)	121.18(6)

Table 5. Bond lengths d (Å) in structure **II**

Bond	d	Bond	d	Bond	d	Bond	d
P(1)–O(11)	1.496(2)	N(1A)–H(1A)	0.89(4)	C(8A)–C(9A)	1.481(5)	C(4B)–C(10B)	1.479(6)
P(1)–O(14)	1.512(3)	C(2A)–O(2A)	1.274(4)	N(1B)–C(9B)	1.359(5)	C(5B)–C(9B)	1.338(5)
P(1)–O(13)	1.542(3)	C(2A)–C(3A)	1.417(5)	N(1B)–C(2B)	1.367(5)	C(5B)–C(6B)	1.498(5)
P(1)–O(12)	1.544(3)	C(3A)–C(4A)	1.370(5)	N(1B)–H(1B)	0.88(4)	C(6B)–C(7B)	1.524(7)
O(12)–H(12)	0.89(7)	C(4A)–C(5A)	1.402(5)	C(2B)–O(2B)	1.271(4)	C(7B)–C(8B)	1.520(7)
O(13)–H(13)	0.94(7)	C(4A)–C(10A)	1.499(5)	C(2B)–C(3B)	1.410(5)	C(8B)–C(9B)	1.508(5)
O(14)–H(14)	0.86(8)	C(5A)–C(9A)	1.358(5)	C(3B)–C(4B)	1.366(5)	C(21)–O(21)	1.387(7)
N(1A)–C(2A)	1.356(5)	C(5A)–C(6A)	1.505(5)	C(4B)–C(5B)	1.424(5)	O(21)–H(21)	0.86(5)
N(1A)–C(9A)	1.359(4)	C(7A)–C(8A)	1.538(6)				

Table 6. Bond angles ω (deg) in structure **II**

Angle	ω	Angle	ω
O(11)–P(1)–O(14)	111.85(17)	C(9A)–C(8A)–C(7A)	102.6(3)
O(11)–P(1)–O(13)	112.07(16)	C(5A)–C(9A)–N(1A)	120.3(3)
O(14)–P(1)–O(13)	109.31(18)	C(5A)–C(9A)–C(8A)	114.6(3)
O(11)–P(1)–O(12)	111.53(16)	N(1A)–C(9A)–C(8A)	125.1(3)
O(14)–P(1)–O(12)	106.88(18)	C(9B)–N(1B)–C(2B)	121.6(3)
O(13)–P(1)–O(12)	104.83(18)	C(9B)–N(1B)–H(1B)	120(2)
P(1)–O(12)–H(12)	113(4)	C(2B)–N(1B)–H(1B)	119(2)
P(1)–O(13)–H(13)	119(4)	O(2B)–C(2B)–N(1B)	117.0(3)
P(1)–O(14)–H(14)	124(5)	O(2B)–C(2B)–C(3B)	126.6(3)
C(2A)–N(1A)–C(9A)	122.8(3)	N(1B)–C(2B)–C(3B)	116.4(3)
C(2A)–N(1A)–H(1A)	119(2)	C(4B)–C(3B)–C(2B)	123.1(4)
C(9A)–N(1A)–H(1A)	119(2)	C(3B)–C(4B)–C(5B)	117.2(4)
O(2A)–C(2A)–N(1A)	119.7(3)	C(3B)–C(4B)–C(10B)	122.6(4)
O(2A)–C(2A)–C(3A)	123.5(3)	C(5B)–C(4B)–C(10B)	120.2(4)
N(1A)–C(2A)–C(3A)	116.9(3)	C(9B)–C(5B)–C(4B)	119.5(3)
C(4A)–C(3A)–C(2A)	121.4(4)	C(9B)–C(5B)–C(6B)	111.4(4)
C(3A)–C(4A)–C(5A)	118.6(3)	C(4B)–C(5B)–C(6B)	129.1(4)
C(3A)–C(4A)–C(10A)	121.5(4)	C(5B)–C(6B)–C(7B)	103.4(4)
C(5A)–C(4A)–C(10A)	119.9(4)	C(8B)–C(7B)–C(6B)	109.4(4)
C(9A)–C(5A)–C(4A)	120.0(3)	C(9B)–C(8B)–C(7B)	102.1(4)
C(9A)–C(5A)–C(6A)	109.8(3)	C(5B)–C(9B)–N(1B)	122.2(3)
C(4A)–C(5A)–C(6A)	130.2(3)	C(5B)–C(9B)–C(8B)	113.4(3)
C(5A)–C(6A)–C(7A)	104.4(3)	N(1B)–C(9B)–C(8B)	124.4(4)
C(6A)–C(7A)–C(8A)	108.3(4)	C(21)–O(21)–H(21)	105(3)

Table 7. Bond lengths d (Å) in structure **IIa**

Bond	d	Bond	d
N(1)–C(2)	1.43(2)	C(4)–C(10)	1.51(2)
N(1)–C(9)	1.37(2)	C(5)–C(6)	1.57(3)
N(1)–H(1)	0.86(7)	C(5)–C(9)	1.34(3)
O(2)–C(2)	1.23(2)	C(6)–C(7)	1.53(2)
C(2)–C(3)	1.41(2)	C(7)–C(8)	1.57(2)
C(3)–C(4)	1.39(2)	C(8)–C(9)	1.46(2)
C(4)–C(5)	1.40(2)		

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

Bond	d	Bond	d
N(1)–C(2)	1.352(3)	C(5)–C(11)	1.383(3)
N(1)–C(11)	1.358(3)	C(5)–C(6)	1.513(4)
N(1)–H(1)	0.839(19)	C(6)–C(7)	1.491(4)
C(2)–O(2)	1.264(3)	C(7)–C(8)	1.501(4)
C(2)–C(3)	1.424(3)	C(8)–C(9)	1.563(4)
C(3)–C(4)	1.382(3)	C(9)–C(10)	1.561(4)
C(4)–C(5)	1.392(3)	C(10)–C(11)	1.467(3)
C(4)–C(12)	1.507(4)		

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

Angle	ω	Angle	ω
C(2)–N(1)–C(11)	124.8(2)	C(11)–C(5)–C(6)	117.5(2)
C(2)–N(1)–H(1)	124.6(13)	C(4)–C(5)–C(6)	124.1(2)
C(11)–N(1)–H(1)	110.6(13)	C(7)–C(6)–C(5)	117.1(2)
O(2)–C(2)–N(1)	121.1(2)	C(6)–C(7)–C(8)	114.8(2)
O(2)–C(2)–C(3)	123.0(2)	C(7)–C(8)–C(9)	116.1(2)
N(1)–C(2)–C(3)	115.9(2)	C(10)–C(9)–C(8)	113.7(2)
C(4)–C(3)–C(2)	120.6(2)	C(11)–C(10)–C(9)	115.1(2)
C(3)–C(4)–C(5)	120.6(2)	N(1)–C(11)–C(5)	119.7(2)
C(3)–C(4)–C(12)	118.2(2)	N(1)–C(11)–C(10)	115.2(2)
C(5)–C(4)–C(12)	121.2(2)	C(5)–C(11)–C(10)	125.1(2)
C(11)–C(5)–C(4)	118.4(2)		

Table 10. Bond lengths d (Å) in structure **IV**

Bond	d	Bond	d
N(1)–C(2)	1.361(3)	C(5)–C(12)	1.361(3)
N(1)–C(12)	1.381(3)	C(5)–C(6)	1.527(3)
N(1)–H(1)	0.82(2)	C(6)–C(7)	1.518(3)
C(2)–O(2)	1.273(3)	C(7)–C(8)	1.519(4)
C(2)–C(3)	1.394(4)	C(8)–C(9)	1.550(4)
C(3)–C(4)	1.355(4)	C(9)–C(10)	1.507(3)
C(4)–C(5)	1.425(3)	C(10)–C(11)	1.540(3)
C(4)–C(13)	1.504(4)	C(11)–C(12)	1.478(3)

Table 11. Bond angles ω (deg) in structure **IV**

Angle	ω	Angle	ω
C(2)–N(1)–C(12)	124.1(2)	C(12)–C(5)–C(6)	120.7(2)
C(2)–N(1)–H(1)	119.8(14)	C(4)–C(5)–C(6)	121.2(2)
C(12)–N(1)–H(1)	116.0(14)	C(7)–C(6)–C(5)	114.8(2)
O(2)–C(2)–N(1)	119.2(2)	C(8)–C(7)–C(6)	117.8(2)
O(2)–C(2)–C(3)	124.9(2)	C(7)–C(8)–C(9)	114.7(2)
N(1)–C(2)–C(3)	115.9(2)	C(10)–C(9)–C(8)	115.8(2)
C(4)–C(3)–C(2)	122.3(2)	C(9)–C(10)–C(11)	115.2(2)
C(3)–C(4)–C(5)	120.2(2)	C(12)–C(11)–C(10)	112.2(2)
C(3)–C(4)–C(13)	119.1(2)	C(5)–C(12)–N(1)	119.6(2)
C(5)–C(4)–C(13)	120.7(2)	C(5)–C(12)–C(11)	125.8(2)
C(12)–C(5)–C(4)	118.0(2)	N(1)–C(12)–C(11)	114.6(2)

Table 12. Bond lengths d (Å) in structure **V**

Bond	d	Bond	d
N(1)–C(2)	1.396(12)	C(5)–C(6)	1.485(12)
N(1)–C(9)	1.346(14)	C(5)–C(10)	1.588(15)
C(2)–O(2)	1.270(13)	C(6)–C(7)	1.452(14)
C(2)–C(3)	1.506(13)	C(7)–C(8)	1.623(18)
C(3)–C(4)	1.463(14)	C(8)–C(9)	1.512(13)
C(3)–C(11)	1.259(12)	C(9)–C(10)	1.254(14)
C(4)–C(10)	1.452(12)	C(11)–N(11)	1.207(9)

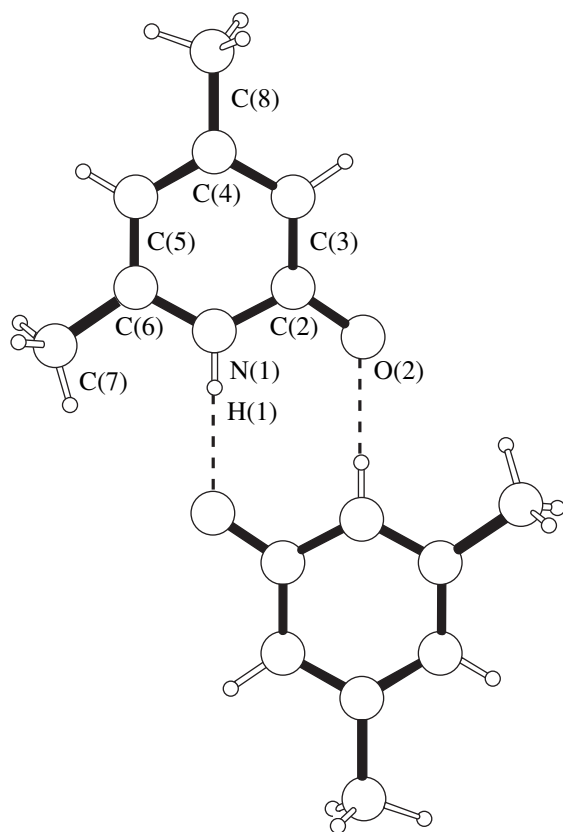
and **IV** were equal to 20%. Compound **V** was prepared according to the procedure described in [16]. Physico-chemical characteristics of the compounds synthesized are listed in Table 1.

The experimental intensities for single crystals of compounds **I–IV** were measured on a CAD4 diffractometer [17] ($\lambda\text{MoK}\alpha$, graphite monochromator, ω scan mode) at room temperature. The unit cell parameters

Table 13. Parameters of the interatomic contacts in the structures studied

<i>D</i> -H	<i>d</i> (<i>D</i> -H)	<i>d</i> (<i>D</i> ⋯ <i>A</i>)	<i>d</i> (H⋯ <i>A</i>)	ω <i>DHA</i>	<i>A</i>	Symmetry code
I						
N(1)-H(1)	0.874(1)	2.768(1)	1.895(5)	176.1(1)	O(2)	(- <i>x</i> ; 1 - <i>y</i> ; 1 - <i>z</i>)
II						
N(1A)-H(1A)	0.89(4)	2.780(4)	1.89(4)	177(4)	O(11)	
N(1B)-H(1B)	0.88(4)	2.768(4)	1.89(4)	173(4)	O(21)	
O(12)-H(12)	0.89(7)	2.548(4)	1.68(7)	168(7)	O(2A)	
O(13)-H(13)	0.94(6)	2.589(4)	1.65(6)	173(6)	O(11)	(- <i>x</i> ; 1 - <i>y</i> ; 1 - <i>z</i>)
O(14)-H(14)	0.86(8)	2.462(4)	1.60(8)	175(8)	O(2B)	(- <i>x</i> ; 1 - <i>y</i> ; 1 - <i>z</i>)
O(21)-H(21)	0.86(5)	2.710(4)	1.86(5)	173(5)	O(2A)	(1 - <i>x</i> ; 1 - <i>y</i> ; 1 - <i>z</i>)
IIa						
N(1)-H(1)	0.86(7)	2.81(1)	2.01(7)	156(7)	O(2)	(1 - <i>x</i> ; <i>y</i> - 1/2; 1/2 - <i>z</i>)
III						
N(1)-H(1)	0.839(19)	2.785(3)	1.96(2)	167(2)	O(2)	(- <i>x</i> ; - <i>y</i> ; 1 - <i>z</i>)
IV						
N(1)-H(1)	0.82(2)	2.776(3)	1.96(2)	174(2)	O(2)	(1 - <i>x</i> ; - <i>y</i> ; 1 - <i>z</i>)
V						
N(1)-H(1)	0.89(5)	2.71(1)	1.83(5)	171(6)	O(2)	(-1 - <i>x</i> ; 1 - <i>y</i> ; - <i>z</i>)

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.

**Fig. 3.** Molecular structure, atomic numbering, and hydrogen bond formation for compound I.

were determined and refined using 25 reflections in the θ range 12° – 15° . No correction for absorption was introduced because of the small linear absorption coefficients of the compounds studied and the small sizes of their crystals. The primary processing of the sets of diffraction data was performed with the WinGX98 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.

The diffraction experiments for compounds **IIa** and **V** (available only in the form of powders) were performed on a DRON-3 automated powder diffractometer (NPO Burevestnik; $\lambda\text{CuK}\alpha$; Ge monochromator; step width, 0.02° in 2θ). The unit cell parameters were determined with the ITO indexing program [20]. The space groups were determined from the systematic absences of the reflections. Preliminary data on the molecular structures of compounds **IIa** and **V** were confirmed by the ^1H NMR spectra. The initial geometrical models were constructed using semiempirical and empirical methods with the MOPAC 6.0 [21] and PCMODEL [22] programs. The structures were solved by the grid search procedure [23] based on the given molecular fragments. The Rietveld full-profile refinement of the structures was performed according to the MRJA program [24]. The pseudo-Voigt function was used as a profile func-

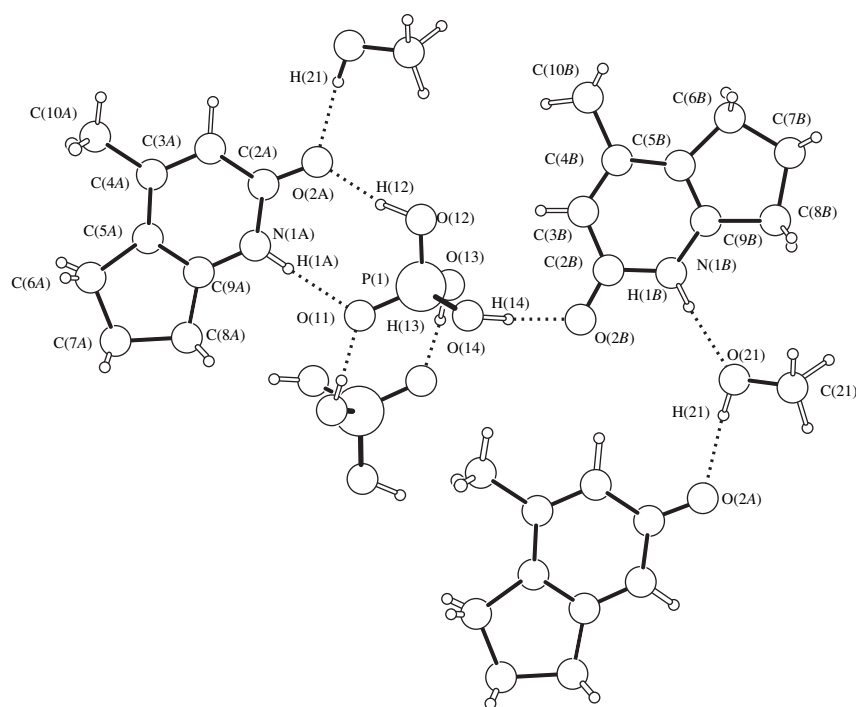


Fig. 4. Molecular structure, atomic numbering, and hydrogen bond formation for compound **II**.

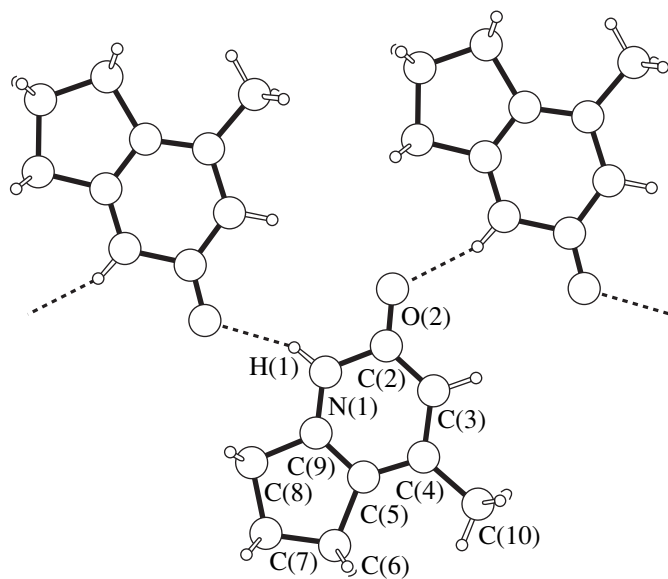


Fig. 5. Molecular structure, atomic numbering, and hydrogen bond formation for compound **IIa**.

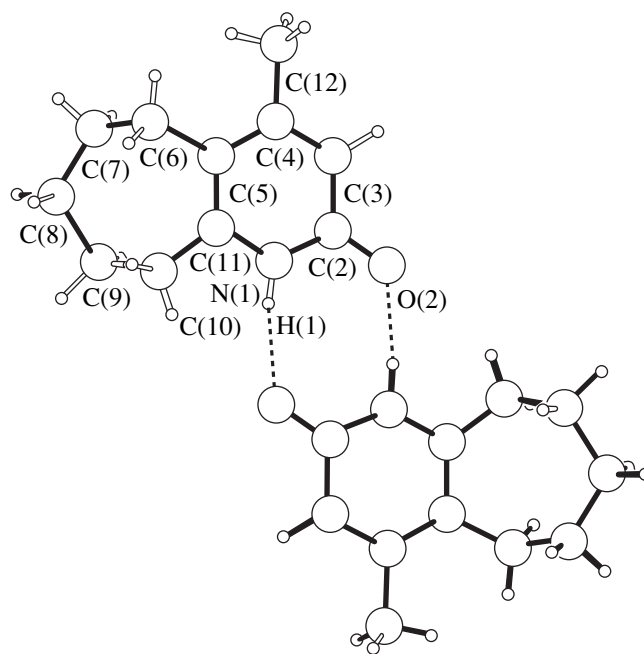


Fig. 6. Molecular structure, atomic numbering, and hydrogen bond formation for compound **III**.

tion, and the background was approximated by the Chebyshev fifth-degree polynomials. The thermal parameters of the non-hydrogen atoms of the molecular skeleton were averaged in the course of refinement.

The main experimental parameters and crystal data for the compounds studied are summarized in Table 2. The interatomic distances and bond angles are listed in Tables 3–12. The experimental and difference X-ray

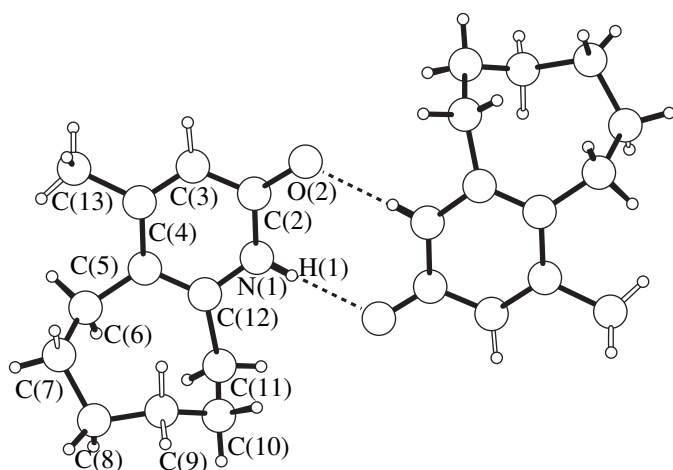


Fig. 7. Molecular structure, atomic numbering, and hydrogen bond formation for compound IV.

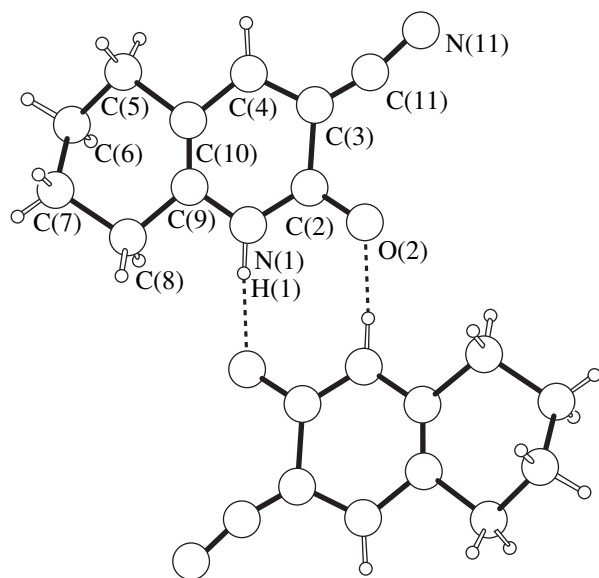


Fig. 8. Molecular structure, atomic numbering, and hydrogen bond formation for compound V.

spectra are shown in Figs. 1 and 2. The molecular structures with the atomic numberings are shown in Figs. 3–8. The drawings were obtained with the PLUTON96 program package [25].

Crystal data for the compounds studied are deposited in the Cambridge Structural Database (deposit nos. 213 170–213 175).

RESULTS AND DISCUSSION

It is common knowledge that 2-pyridones and their salts act as ambident compounds in reactions with electrophilic agents, for example, in alkylation reactions. The methyl group or the methylene link in the 6-position of 2-pyridone substantially affects the selectivity

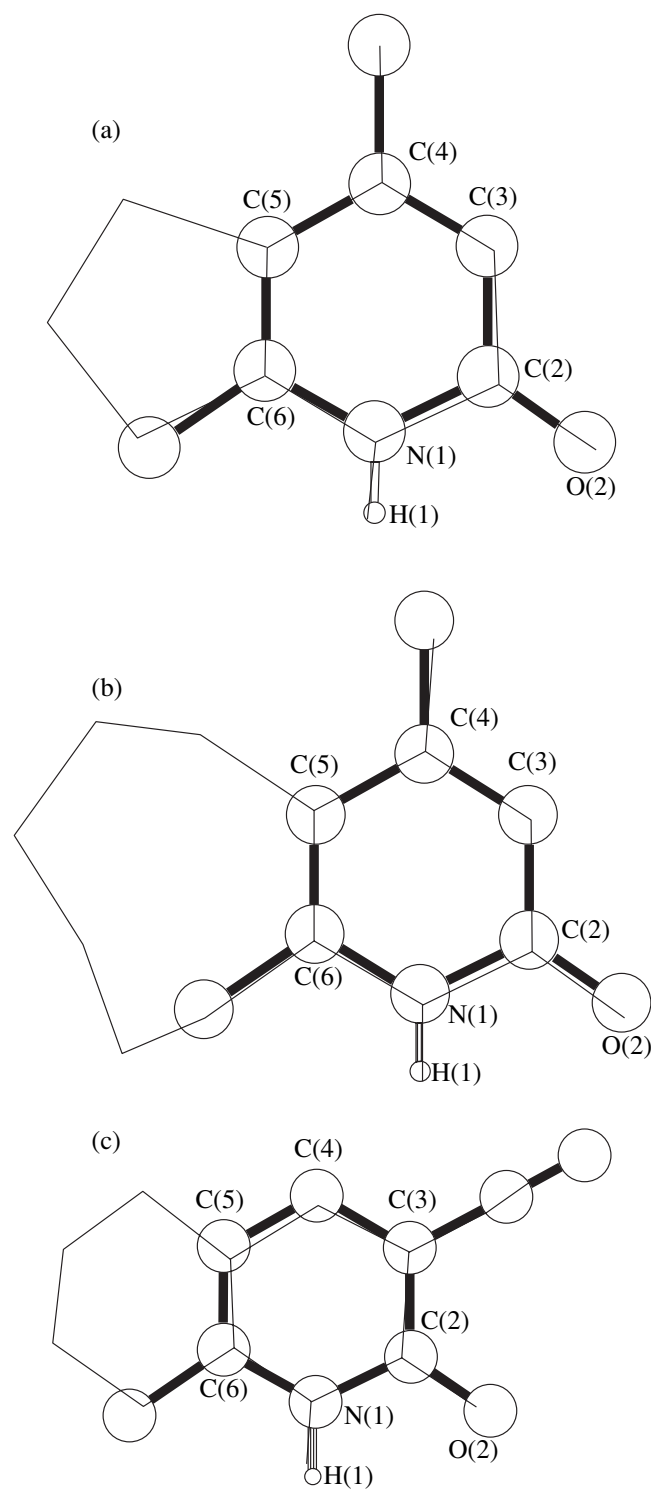


Fig. 9. Superposition of molecules: (a) I and IIa, (b) I and IV, and (c) VII and V.

of these reactions due to steric shielding of the nitrogen atom by the alkyl fragment. In this connection, it is of interest to determine the degree of steric shielding upon replacement of the methyl group by a cycloalkane frag-

ment that has a different size and is annelated to the C(5)–C(6) bond. The structural data for the compound with the cyclohexane fragment [2-oxo-1,2,5,6,7,8-hexahydroquinoline (**VI**)] were obtained earlier in [11]. The structure of cyanoderivative **V** was compared with that of its prototype, namely, 3-cyano-6-methylpyridin-2(1*H*)-one (**VII**), which was described in [26].

The simplest way to compare the structural transformations observed when going from the methyl group to the cycloalkane fragment in molecules **I–VII** is to superpose the structure of the pyridone fragment of the prototype molecule **I** and those of derivatives **II–V** and to compare the relative positions of the 6-CH₃ group and the methylene link in the 6-position (Fig. 9). It is clearly seen that the degree of shielding decreases only in the case of cyclopentane derivative **IIa** (the steric strain tightens the five-membered ring removing the methylene link in the 6-position from the nitrogen atom; Fig. 9a). In all other derivatives (Fig. 9b), the positions of the methylene links in the six-, seven-, and eight-membered rings almost exactly coincide with the position of the methyl group in the parent molecule **I**. A similar situation is observed when going from the methyl to cyclohexane derivative in 3-cyanopyridones **V** and **VII** (Fig. 9c).

Compounds **I–V** form hydrogen-bond systems, which are inherent attributes of crystal structures in this class of compounds. In compounds **I** and **III–V**, centrosymmetric eight-membered dimers involving the H(1)N(1)C(2)O(2) atoms of the pyridone ring are formed (Table 13, Figs. 3, 6–8).

Molecule **IIa** provides an exception to the rule of the formation of eight-membered cyclic dimers. In this compound, the pyridone atoms H(1), N(1), and O(2) are also involved in hydrogen bonding but the type of binding is different: in the crystal structure, infinite chains are formed instead of dimeric fragments (Fig. 5). Compound **II** is characterized by a more extended hydrogen-bond system, which includes not only heterocyclic molecules but also molecules of orthophosphoric acid and solvate methanol. Figure 4 shows that, in the crystal structure, dimeric fragments are formed only via the hydrogen bonds of H₃PO₄ molecules. The hydrogen bonds formed by two crystallographically independent pyridone molecules (*A* and *B*) are different in type. Molecule *A* forms three hydrogen bonds, namely, two bonds with H₃PO₄ and one bond with the methanol molecule. Molecule *B* forms only two hydrogen bonds, namely, one bond with H₃PO₄ and one bond with the methanol molecule. Note that the solvate molecule acts as both a donor and an acceptor (Table 13). The parameters of the hydrogen bonds were calculated using the PARST95 program [27].

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