

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL AND MOLECULAR STRUCTURE OF TWO NEW SCHIFF BASES:
PAEONOL—ETHYLENEDIAMINE AND PAEONOL—1,3-PROPYLENEDIAMINE© 2007 Т.-Т. Ху¹, Х.-Y. Ху², J. Gao³, Sh.-Sh. Ni², D.-Q. Wang⁴,
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Two new Schiff bases were prepared by the condensation reaction of paeonol with ethylenediamine (for compound **1**) and 1,3-propylenediamine (for compound **2**). The compounds were studied with single crystal X-ray diffraction method. Compound **1** is monoclinic, space group $P2_1/c$, $a = 10.956(15)$, $b = 6.767(10)$, $c = 12.494(18)$ Å; $\beta = 104.66(2)^\circ$, $V = 896(2)$ Å³, $Z = 2$. Compound **2** is triclinic, space group $P-1$, $a = 6.878(2)$, $b = 12.141(4)$, $c = 12.414(4)$ Å; $\alpha = 101.023(6)^\circ$, $\beta = 103.415(6)^\circ$, $\gamma = 102.337(6)^\circ$, $V = 952.8(6)$ Å³, $Z = 2$. The molecular structures of **1** and **2** are similar; the molecule being centrosymmetric in **1** but asymmetric in **2**.

Keywords: Molecular crystals, crystal structure, amine, 2-hydroxy-4-methoxyacetophenone.

Paeonol, 2-hydroxy-4-methoxyacetophenone, is a component widely used in Chinese traditional medicine. It has been reported to possess analgesic, sedative, antiallergic, antioxidative and antimicrobial properties and has been used as a remedy for cardiovascular and female genital diseases [1–5]. The ramifications of paeonol have attracted considerable attention because of their potential biological properties and catalytic activity [6–8]. Recently, several new derivatives of paeonol were prepared and characterized but only few crystal structures of the compounds have been reported. The information about the Schiff bases of paeonol is still very scanty [9, 10]. This communication reports the synthesis and crystal structure of two new Schiff bases, paeonol—ethylenediamine (**1**) and paeonol—1,3-propylenediamine (**2**).

Experimental. Synthesis of paeonol—ethylenediamine (1). A solution of ethylenediamine (5 mmol) in absolute methanol (15 ml) was added dropwise to a stirred solution of paeonol (10 mmol) in absolute methanol (20 ml). After stirring for 4 h at 50 °C, the precipitated product was separated by filtration, washed with small amounts of methanol and dried in vacuum. Yield 71 %. M. p. 247 °C (dec.). Anal. Calcd. for C₂₀H₂₄N₂O₄ (%): C 67.34, H 6.73, N 7.86. Found: C 67.31, H 6.76, N 7.81. IR (cm⁻¹, KBr): 3524 s $\nu(\text{OH})$; 1595 s $\nu(\text{C}=\text{N})$; 2938, 2843 s $\nu(\text{CH}_2)$; 1346, 1239 m $\nu(\text{benzene ring})$. Yellow single crystals of the complex suitable for X-ray structure determination were obtained by slow evaporation of the filtrate for about five days at ambient temperature.

Synthesis of paeonol—1,3-propylenediamine (2). A solution of 1,3-propylenediamine (5 mmol) in absolute methanol (20 ml) was added dropwise to a stirred solution of paeonol (10 mmol) in absolute methanol (20 ml). After stirring for 4 h at 65 °C, the precipitated product was separated by filtration, washed with small amounts of methanol and dried in vacuum. Yield 78 %. M. p. 175 °C (dec.). Anal. Calcd. for C₂₁H₂₆N₂O₄ (%): C 68.03, H 7.02, N 7.56. Found: C 68.07, H 6.99, N 7.59. IR (cm⁻¹,

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Table 1

Crystal Data and Details of Experiment for **1** and **2**

Parameter	1	2
Formula	C ₂₀ H ₂₄ N ₂ O ₄	C ₂₁ H ₂₆ N ₂ O ₄
Molecular weight	356.41	370.44
Crystal size, mm	0.27 × 0.21 × 0.06	0.35 × 0.18 × 0.10
Space group, <i>Z</i>	<i>P</i> 2 ₁ / <i>c</i> , 2	<i>P</i> -1, 2
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.956(15), 6.767(10), 12.494(18)	6.878(2), 12.141(4), 12.414(4)
α , β , γ , deg.	90, 104.66(2), 90	101.023(6), 103.415(6), 102.337(6)
<i>V</i> , Å ³	896(2)	952.8(6)
ρ_{calc} , g/cm ³	1.321	1.291
μ , mm ⁻¹	0.092	0.090
All reflections	4484	5035
Independent reflections	1791	3318
Intense reflections (<i>I</i> > 2 σ (<i>I</i>))	788	1272
Refined parameters	118	244
<i>R</i> 1, <i>wR</i> 2 (intense reflections)	0.058, 0.146	0.068, 0.140
<i>wR</i> 2 (independent reflections)	0.182	0.182
GOOF	1.012	0.998
CCDC deposition number	600770	600771

KBr): 3072 s ν (OH); 1603 s ν (C=N); 2934, 2836 s ν (CH₂); 1214, 1142 m ν (benzene ring). Yellow single crystals of the complex suitable for X-ray structure determination were obtained by slow evaporation of the filtrate for about two days at ambient temperature.

X-Ray diffraction study. The intensity data were collected on a SMART APEX CCD diffractometer at room temperature (ω -2 θ scan mode, graphite monochromated MoK α radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined anisotropically using the least-squares technique implemented in the SHELX-97 package [11, 12]. All hydrogen atoms were added according to theoretical models. The unit cell parameters and experimental details are given in Table 1. Full crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC) and are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html; CCDC deposition numbers are given in Table 1.

Results and Discussion. Essential crystallographic information on the compounds studied is given in Tables 1–3. The molecular structure and crystal packing of compounds **1** and **2** are illustrated in Figs. 1 and 2.

Table 2

Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **1** and **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
1	2	3	4	5	6	7	8	9	10
1									
C(1)	4038(3)	9428(5)	8428(3)	46(1)	C(8)	2398(3)	8592(5)	6182(3)	42(1)
C(2)	3689(3)	7385(5)	8014(3)	36(1)	C(9)	523(4)	4274(6)	3178(3)	66(1)
C(3)	2903(3)	7045(5)	6897(3)	36(1)	C(10)	4903(3)	6016(5)	9741(3)	44(1)
C(4)	2631(3)	5081(5)	6493(3)	38(1)	N(1)	4084(3)	5839(4)	8621(2)	42(1)
C(5)	1924(3)	4775(5)	5401(3)	44(1)	O(1)	3042(2)	3516(4)	7111(2)	57(1)
C(6)	1475(3)	6344(5)	4725(3)	42(1)	O(2)	808(2)	6200(4)	3654(2)	59(1)
C(7)	1701(3)	8279(6)	5128(3)	50(1)					

О к о н ч а н и е т а б л . 2

1	2	3	4	5	6	7	8	9	10
2									
N(1)	-1327(5)	8830(3)	7842(3)	43(1)	C(9)	2703(8)	14727(4)	10645(4)	79(2)
N(2)	1492(6)	7613(3)	5247(3)	47(1)	C(10)	1676(8)	9134(4)	4215(4)	67(2)
O(1)	1696(4)	10592(3)	8619(2)	55(1)	C(11)	2225(7)	8082(4)	4525(4)	45(1)
O(2)	769(6)	14065(3)	10686(3)	69(1)	C(12)	3616(7)	7555(4)	4020(3)	42(1)
O(3)	3240(5)	6029(2)	4982(2)	55(1)	C(13)	4076(7)	6530(4)	4272(3)	40(1)
O(4)	7684(5)	6114(3)	2567(2)	60(1)	C(14)	5433(7)	6041(4)	3802(3)	46(1)
C(1)	4742(7)	8776(4)	8135(4)	62(1)	C(15)	6337(7)	6531(4)	3075(3)	45(1)
C(2)	-2506(7)	9367(4)	8286(3)	41(1)	C(16)	5932(7)	7538(4)	2808(3)	50(1)
C(3)	-1611(7)	10571(4)	8932(3)	36(1)	C(17)	4605(7)	8027(4)	3267(3)	52(1)
C(4)	478(7)	11135(4)	9050(3)	43(1)	C(18)	8251(8)	5111(4)	2836(4)	71(2)
C(5)	1299(7)	12311(4)	9627(3)	47(1)	C(19)	-2092(7)	7629(4)	7140(3)	52(1)
C(6)	88(8)	12915(4)	10102(3)	47(1)	C(20)	-489(7)	7300(4)	6595(3)	50(1)
C(7)	-1930(8)	12371(4)	10019(4)	51(1)	C(21)	67(7)	8045(4)	5811(3)	50(1)
C(8)	-2761(7)	11229(4)	9438(4)	49(1)					

Table 3

Bond Lengths d , Å and Angles ω , deg. for **1** and **2**

1					
Bond	d	Bond	d	Bond	d
N(1)—C(2)	1.300(4)	N(1)—C(10)	1.464(4)	O(1)—C(4)	1.321(4)
O(2)—C(6)	1.356(4)	O(2)—C(9)	1.434(5)	C(2)—C(3)	1.461(5)
C(10)—C(10)#1	1.512(7)				
Angle	ω	Angle	ω	Angle	ω
C(2)—N(1)—C(10)	121.7(3)	C(6)—O(2)—C(9)	118.7(3)	N(1)—C(2)—C(3)	117.3(3)
C(3)—C(2)—C(1)	121.0(3)	O(2)—C(6)—C(5)	125.0(3)	C(8)—C(3)—C(2)	122.4(3)
O(1)—C(4)—C(5)	118.2(3)	O(1)—C(4)—C(3)	122.0(3)	O(2)—C(6)—C(7)	115.1(3)
2					
Bond	d	Bond	d	Bond	d
N(1)—C(2)	1.297(5)	O(2)—C(9)	1.417(5)	O(3)—C(13)	1.329(4)
N(1)—C(19)	1.461(5)	O(4)—C(18)	1.429(5)	O(1)—C(4)	1.316(5)
N(2)—C(11)	1.289(5)	N(2)—C(21)	1.457(5)		
Angle	ω	Angle	ω	Angle	ω
C(2)—N(1)—C(19)	122.5(4)	N(2)—C(21)—C(20)	109.7(4)	N(2)—C(11)—C(10)	121.7(4)
C(11)—N(2)—C(21)	123.3(4)	C(8)—C(3)—C(2)	122.3(4)	C(17)—C(12)—C(11)	122.7(4)
N(1)—C(2)—C(3)	118.0(4)	O(1)—C(4)—C(5)	117.9(4)	O(3)—C(13)—C(14)	118.5(4)
N(1)—C(2)—C(1)	121.8(4)	O(2)—C(6)—C(7)	115.3(4)	C(14)—C(15)—O(4)	124.9(4)

In the crystal structure, the molecule of **1** is centrosymmetric (Fig. 1, *a*). As evident from Table 3, most of the bond lengths correspond to expected values ranging from a single to double bond. The bond lengths C(2)—N(1) of 1.300 Å and C(10)—N(1) of 1.464 Å are typical for C=N Schiff base bond and C—N single bond, respectively [13]. Compared to the normal phenol C—O bond distance of 1.362 Å, a shorter C(11)—O(1) bond distance of 1.321 Å may be owing to the effect of hyperconjugation [14]. Due to the centrosymmetry of the molecule, plane A composed of atoms C(1)—C(8),

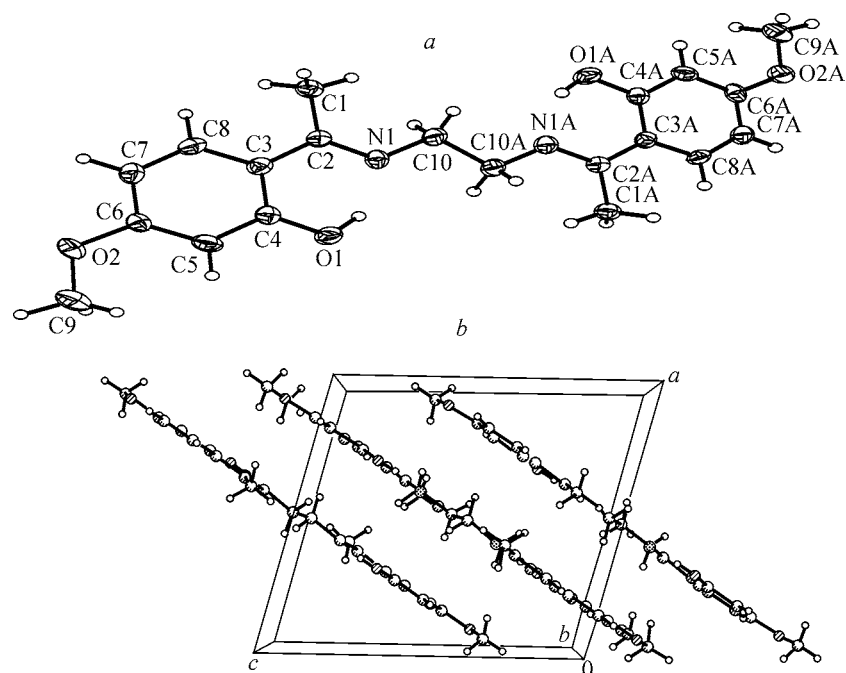


Fig. 1. Molecular structure (a) and crystal packing (b) for compound 1

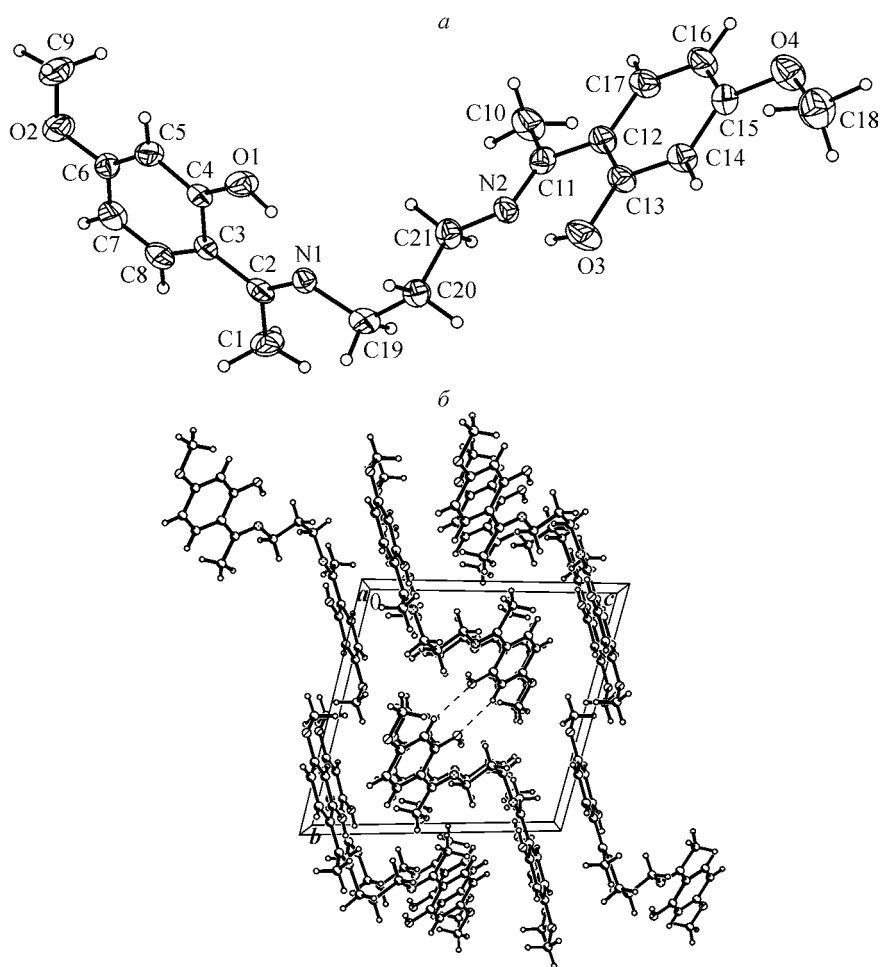


Fig. 2. Molecular structure (a) and crystal packing (b) for compound 2

Table 4

Hydrogen Bonds Geometry (Distances, Å; Angles, deg.)

Compound	Bond D—H...A	D—H	H...A	D...A	D—H...A
1	O(1)—H(1)...N(1)	0.82	1.764	2.498	148.23
2	O(1)—H(1)...N(1)	0.82	1.759	2.492	147.96
2	O(3)—H(3)...N(3)	0.82	1.748	2.486	148.82

C(10), O(1) and N(1) is coplanar with the related plane B composed of atoms C(1A)—C(8A), C(10A), O(1A) and N(1A) and, therefore, a coplanar conjugation system may form. The packing diagram for the crystal is shown in Fig. 1, *b*. The crystal structure is layer-like and it is controlled by intermolecular van der Waals forces and intramolecular hydrogen bonds between O(1) and N(1) atoms (Table 4).

In contrast to **1**, compound **2** reveals an asymmetric molecule in the crystal structure. In overall comparison, the molecular structure of **2** is similar to that of **1** but some differences in bond lengths and angles may be noticed. The bond length C(2)—N(1) of 1.279 Å, C(11)—N(2) of 1.289 Å and C(19)—N(1) of 1.461 Å, C(21)—N(2) of 1.457 Å are typical for C=N Schiff base bond and C—N single bond, respectively [13]. The packing diagram for the compound **2** shows that every molecule is linked to others by intermolecular van der Waals forces and both intramolecular (Table 4) and intermolecular (Fig. 2, *b*) hydrogen bonds, with the resulting packing mode being quite different from that found in **1**.

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