Formation of H-bonded ionic associates in reactions of 5-nitrosalicylaldehyde with secondary amines

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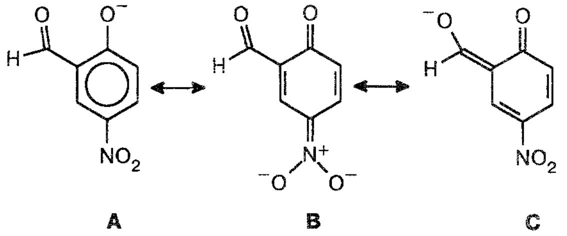
5-Nitrosalicylaldehyde reacts with highly basic secondary aliphatic amines to form molecular complexes of 1 : 1 composition. The complexes with piperidine, diethylamine, dipentylamine, and dibenzylamine (**1—4**, respectively) have been obtained in the crystalline state and characterized. The X-ray diffraction structural analysis of complex **1** demonstrated that it exists in a crystal as an H-bonded dimeric ionic associate $[C_5H_{12}N^+ \cdot C_7H_4NO_4^-]_2$ formed as a result of the transfer of the phenyl proton of the aldehyde to the piperidine N atom. According to the results of IR spectroscopy, the other complexes obtained have similar structures.

Key words: 5-nitrosalicylaldehyde; secondary amines; aminals; H-bonded ionic associates, X-ray structural analysis.

Aminals, the products of the condensation of carbonyl compounds with secondary amines, are stable compounds; their formation proceeds without complications even when the amount of the amine used was less than stoichiometric.[1] Previously, we have demonstrated[2] that boiling of salicylaldehyde with an excess of morpholine (or piperidine) in propanol during 10 min and subsequent cooling result in progressive formation of morpholinal (or piperidinal) in 90 % (50 %) yield. When hot solutions of the components in isopropanol were mixed, morpholinal of 5-nitrosalicylaldehyde was formed in 96 % yield during 1 h.[3]

However, an attempt to obtain piperidinal of 5-nitrosalicylaldehyde gave an unexpected result. Under conditions of the formation of morpholinal (*i.e.*, when hot solutions of aldehyde and piperidine in isopropanol are mixed) and even on boiling of a solution of aldehyde in an excess of piperidine, the same crystalline product was formed; in the IR spectrum of this compound, the doublet is shifted by ~20 cm^{-1} to the region of higher frequencies compared to the spectrum of the initial aldehyde. Elemental analysis indicated that only one piperidine molecule is involved in the compound. X-ray structural analysis demonstrated that this compound is the 1 : 1 adduct of 5-nitrosalicylaldehyde and piperidine, which exists in the crystal in the form of H-bonded dimeric ionic associate $[C_5H_{12}N^+ \cdot C_7H_4NO_4^-]_2$ (**1**) with a noncrystallographic center of symmetry (Fig. 1 and Tables 1 and 2).

Analysis of the electron density difference Fourier syntheses and bond angles within the moderate accuracy (because of the quality of the crystals) of the experimental data (geometric parameter averaged over two symmetrically independent structural units of compound **1** are given below) points to the proton transfer from the hydroxyl group of the salicylaldehyde molecule to the N atom of the piperidine molecule. In the structure of the anion, the contribution of two quinoid resonance forms **B** and **C** along with the canonical form **A** was observed, which is indicative of a substantial delocalization of the negative charge.



The C(3)—C(4) and C(5)—C(6) bond lengths in the structure of **1** are decreased to 1.35(1) and 1.37(1) Å, respectively, compared to the C(1)—C(2) [1.44(1) Å], C(2)—C(3) [1.44(1) Å], C(4)—C(5) [1.39(1) Å], and C(1)—C(6) [1.39(1) Å] bond lengths, while the C(2)—O(2) bond length [1.27(1) Å] (see Table 1), which exceeds the mean-statistical value for the double C=O

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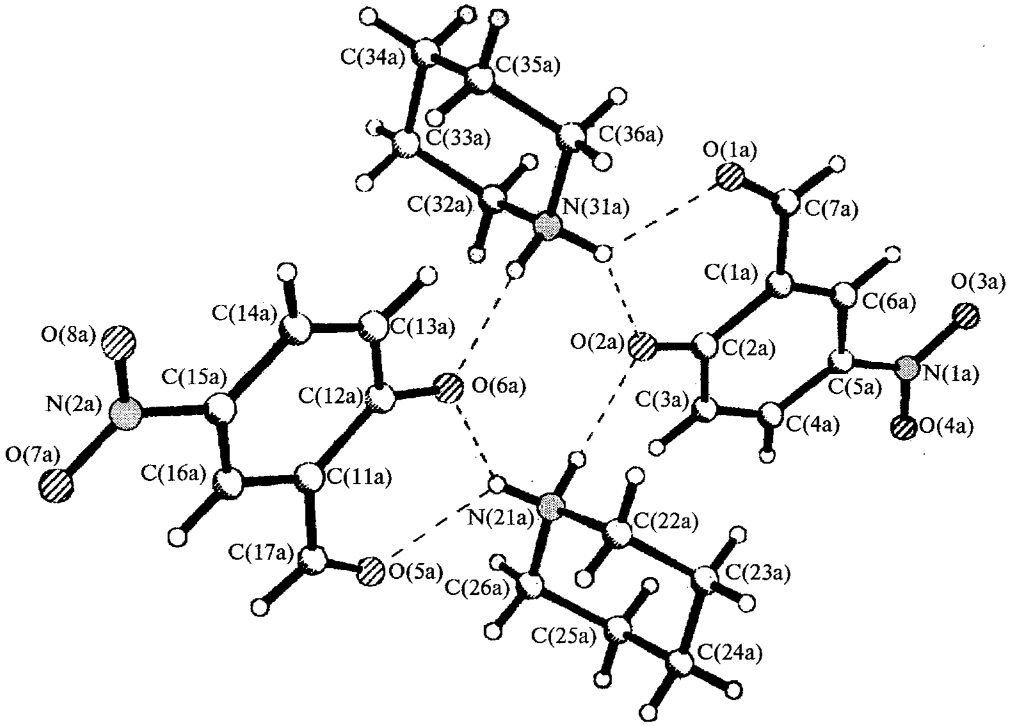

Fig. 1. The overall view of the dimeric ionic associate in the structure of **1**.

bond (1.21 Å),[4] is substantially smaller than the mean-statistical value for the C(Ar)—O single bond (1.36 Å). The endocyclic C(1)—C(2)—C(3) bond angle opposite to the C=O group [115.2(9)°, see Table 1] is slightly shortened compared to the ideal value (120°) in accordance with the π-electron-donating properties of the substituent in the benzene ring.[5]

A sharp difference observed in the behavior of morpholine and piperidine was all the more unexpected because these amines are structural analogs. However, despite the outward similarity, a difference in their basicity is observed, which is almost as large as three orders of magnitude ($\mathrm{p}K_a$ = 8.33 for morpholine and 11.12 for piperidine).[6] Therefore, less basic morpholine enters into the normal reaction with the aldehyde group, while substantially more basic piperidine deprotonates the phenol hydroxyl. Because of the drastically reduced electrophilicity of the aldehyde C atom in the resulting anion (the resonance form **B**), this group is incapable of further reacting with amine.

In turn, the ability of 5-nitrosalicylaldehyde to be deprotonated with highly basic amines is determined by the presence of electron-withdrawing substituents, such as nitro and formyl groups in the *para* and *ortho* positions.

As observed previously, the derivatives of salicylaldehyde and nitrogen bases form salts containing an anion and a cation H-bonded to form a complex: the 1 : 1 complex of 3,5-dichlorosalicylaldehyde with H-aminopyridine monohydrate (**5**) (see Ref. 7) and the 2 : 1

Table 1. Bond lengths (*d*) in the structure of **1**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
O(1)—C(7)	1.20(2)	O(5)—C(17)	1.21(1)	N(21)—C(22)	1.50(1)
O(2)—C(2)	1.27(1)	O(6)—C(12)	1.28(1)	N(21)—C(26)	1.52(2)
O(3)—N(1)	1.25(1)	O(7)—N(2)	1.21(1)	C(22)—C(23)	1.50(2)
O(4)—N(1)	1.25(2)	O(8)—N(2)	1.21(2)	C(23)—C(24)	1.50(2)
N(1)—C(5)	1.42(1)	N(2)—C(15)	1.47(1)	C(24)—C(25)	1.50(2)
C(1)—C(2)	1.45(1)	C(11)—C(12)	1.42(2)	C(25)—C(26)	1.50(2)
C(1)—C(6)	1.37(1)	C(11)—C(16)	1.40(2)	N(31)—C(32)	1.46(1)
C(1)—C(7)	1.47(1)	C(11)—C(17)	1.48(2)	N(31)—C(36)	1.51(2)
C(2)—C(3)	1.43(2)	C(12)—C(13)	1.45(2)	C(32)—C(33)	1.51(2)
C(3)—C(4)	1.36(2)	C(13)—C(14)	1.34(1)	C(33)—C(34)	1.52(2)
C(4)—C(5)	1.40(2)	C(14)—C(15)	1.38(2)	C(34)—C(35)	1.51(2)
C(5)—C(6)	1.39(2)	C(15)—C(16)	1.35(2)	C(35)—C(36)	1.52(2)

Table 2. Bond angles (ω) in the structure of **1**

Angle	ω/deg
O(3)—N(1)—O(4)	121.9(11)
O(3)—N(1)—C(5)	119.6(11)
O(4)—N(1)—C(5)	118.4(10)
C(2)—C(1)—C(6)	119.2(7)
C(2)—C(1)—C(7)	124.1(9)
C(6)—C(1)—C(7)	116.5(9)
O(2)—C(2)—C(1)	123.0(10)
O(2)—C(2)—C(3)	120.5(10)
C(1)—C(2)—C(3)	116.5(9)
C(2)—C(3)—C(4)	122.4(11)
C(3)—C(4)—C(5)	120.2(11)
N(1)—C(5)—C(4)	120.8(10)
N(1)—C(5)—C(6)	120.4(10)
C(4)—C(5)—C(6)	118.8(9)
C(1)—C(6)—C(5)	122.8(9)
O(1)—C(7)—C(1)	126.1(12)
O(7)—N(2)—O(8)	122.8(10)
O(7)—N(2)—C(15)	119.1(11)
O(8)—N(2)—C(15)	118.1(9)
C(12)—C(11)—C(16)	121.7(10)
C(12)—C(11)—C(17)	122.9(9)
C(16)—C(11)—C(17)	115.4(9)
O(6)—C(12)—C(11)	125.3(10)
O(6)—C(12)—C(13)	120.6(9)
C(11)—C(12)—C(13)	114.0(9)
C(12)—C(13)—C(14)	123.4(10)
C(13)—C(14)—C(15)	118.9(11)
N(2)—C(15)—C(14)	119.3(10)
N(2)—C(15)—C(16)	118.6(10)
C(14)—C(15)—C(16)	122.1(10)
C(11)—C(16)—C(15)	119.6(9)
O(5)—C(17)—C(11)	128.0(10)
C(22)—N(21)—C(26)	114.2(9)
N(21)—C(22)—C(23)	110.8(10)
C(22)—C(23)—C(24)	111.6(11)
C(23)—C(24)—C(25)	109.3(10)
C(24)—C(25)—C(26)	113.1(11)
N(21)—C(26)—C(25)	109.7(10)
C(32)—N(31)—C(36)	111.3(8)
N(31)—C(32)—C(33)	112.7(9)
C(32)—C(33)—C(34)	112.4(10)
C(33)—C(34)—C(35)	109.9(10)
C(34)—C(35)—C(36)	110.0(10)
N(31)—C(36)—C(35)	112.3(9)

complex of 2,5-diformyl-4-methylphenol with diaza-18-crown-6 (**6**) (see Ref. 8) were studied. The contribution of the quinoid structure to the anions of complexes **5** and **6** is less pronounced (in particular, the C—O bond length is 1.316(6) Å in structure **5** and 1.288(3) Å in structure **6** compared to 1.27(1) Å in **1**). The geometric parameters of hydrogen bonds O(1)...H(31a)—N(31) [O...N, 2.88(1) Å; O...H, 2.2(1) Å; O...H—N angle, 127(9)°]; O(2)...H(31a)—N(31) [O...N, 2.89(1) Å; O...H, 2.1(1) Å; O...H—N angle, 137(9)°] and O(2)...H(21b)—N(21) [O...N, 2.79(1) Å; O...H, 1.9(1) Å; O...H—N angle, 167(9)°] in structure **1** compared to the parameters of O...H—N determined in complex **5** (O...N, 2.75(2) Å; O...H, 1.8(1) Å; O...H—N angle, 163(10)°) and the parameters of O...H—N in structure **6** (O...N, 2.576(3) Å; O...H—N angle, 167(2)°) correlate with the C—O bond length of the deprotonated group: the shorter the O...N hydrogen bond, the longer the C—O bond.

The anion in structure **1** is essentially planar (deviations of nonhydrogen atoms from their mean plane are no greater than 0.02 Å). The piperidinium cation has a nearly ideal chair conformation (the absolute values of the torsion angles are in the range 50(1)—59(1)°). The remaining geometric parameters of structure **1** are within normal ranges (see Tables 1 and 2).

A similar behavior should also be expected from other highly basic secondary amines. The reactions of 5-nitrosalicylaldehyde with diethylamine ($pK_a = 11.09$),[6] dipentylamine, and dibenzylamine were studied. It was found that all these reactions afford 1 : 1 adducts (**2—4**, respectively), which readily crystallize and have closely similar and typical IR spectra: doublets of stretching bands of the carbonyl group in the region 1700—1680 cm^{-1} and a series of bands apparently due to the N—H and O—H stretching vibrations in the region 3050—2300 cm^{-1}.

Compounds **1—4** are rather stable in air under normal conditions; however, they change color when stored in the light. These compounds, having exact stoichiometry, melt in wide temperature ranges even in the analytically pure state.

Experimental

IR spectra were recorded on a Specord IR-75 instrument in vaseline oil.

Piperidinium 2-formyl-4-nitrophenolate (1). 5-Nitrosalicylaldehyde (10 g, 0.06 mol) was dissolved in isopropanol (35 mL) upon heating, then piperidine (10 mL) was added (bubbling up, reddening), and the mixture was kept for 12 h. When rubbed with a stick, the viscous red solution that formed yielded crystals throughout the volume. Ether and isopropanol were added, and the crystalline material was transferred on a filter, washed with an 1 : 1 ether—isopropanol mixture and petroleum ether, and dried. The yield was ~15 g (quantitative yield). The orange crystals obtained had m.p. 95—117 °C (from toluene). Found (%): C, 56.80; H, 6.00; N, 11.51. $C_{12}H_{16}N_2O_4$. Calculated (%): C, 57.14; H, 6.35; N, 11.11. IR, ν/cm^{-1}: 3054, 2714, 2527, 2434 (NH, OH); 1700, 1687 (C=O).

Diethylammonium 2-formyl-4-nitrophenolate (2). Diethylamine (1 mL) was added to a suspension of 5-nitrosalicylaldehyde (0.8 g, 0.005 mol) in isopropanol (5 mL), and the mixture was heated to the boil. The dark-red solution formed was cooled with ice water, and the crystalline precipitate formed was filtered off, washed with ether, and dried. Orange crystals (0.7 g) were obtained. Additional crystals (0.1 g) were precipitated from the filtrate with ether and isooctane. The

Table 3. Coordinates for nonhydrogen atoms ($\times 10^4$) in the structure of **1**

Atom	*x*	*y*	*z*
O(1)	4634(4)	6748(12)	−1131(5)
O(2)	5317(3)	6266(10)	221(5)
O(3)	2104(4)	6840(11)	906(6)
O(4)	2547(5)	6664(13)	1978(6)
N(1)	2621(6)	6747(12)	1316(6)
C(1)	4079(5)	6560(14)	0
C(2)	4696(6)	6514(15)	455(6)
C(3)	4570(6)	6658(14)	1202(6)
C(4)	3908(6)	6731(14)	1480(7)
C(5)	3315(5)	6674(13)	1032(6)
C(6)	3419(6)	6641(13)	303(7)
C(7)	4109(8)	6706(15)	−777(7)
O(5)	2885(4)	1204(11)	962(5)
O(6)	2228(3)	440(10)	−399(5)
O(7)	5339(4)	2638(11)	−1111(6)
O(8)	4895(5)	2529(12)	−2150(5)
N(2)	4844(5)	2398(13)	−1510(6)
C(11)	3424(6)	1404(14)	−201(5)
C(12)	2833(5)	939(13)	−630(6)
C(13)	2953(5)	1189(15)	−1385(6)
C(14)	3584(5)	1631(14)	−1663(6)
C(15)	4148(6)	1948(12)	−1210(6)
C(16)	4078(5)	1879(13)	−499(6)
C(17)	3390(5)	1486(15)	584(6)
N(21)	1372(4)	870(11)	877(5)
C(22)	1182(7)	2770(14)	572(7)
C(23)	569(7)	3620(16)	961(7)
C(24)	713(8)	3766(17)	1745(8)
C(25)	867(7)	1824(17)	2035(7)
C(26)	1483(7)	877(17)	1678(6)
N(31)	−6153(4)	3350(10)	−1042(5)
C(32)	−6280(6)	1412(15)	−794(6)
C(33)	6869(7)	−443(16)	−1193(8)
C(34)	6756(7)	−479(16)	−1993(7)
C(35)	−6655(7)	2493(16)	−2241(7)
C(36)	−6045(6)	3410(17)	−1838(6)

total yield was 0.8 g (70 %), m.p. 95—112 °C (from toluene). Found (%): C, 55.32; H, 6.34; N, 11.52. $C_{11}H_{16}N_2O_4$. Calculated (%): C, 55.00; H, 6.67; N, 11.67. IR, ν/cm^{-1}: 3040, 2727, 2480, 2394, 2374 (NH, OH); 1700, 1687 (C=O).

Dipentylammonium 2-formyl-4-nitrophenolate (3). 5-Nitrosalicylaldehyde (1 g, 0.006 mol) was dissolved in toluene (5 mL) with heating, dipentylamine (1 mL) was added, and the dark-red mixture was brought to boiling and then cooled with ice water. The crystalline precipitate formed upon rubbing with a glass stick was filtered off, washed with toluene and hexane, and dried on a filter. The yield was 1.58 g (81 %). Light-yellow crystals were obtained, m.p. 55—67 °C (from toluene). Found (%): C, 62.80; H, 8.55; N, 8.70. $C_{17}H_{30}N_2O_4$. Calculated (%): C, 62.58; H, 9.20; N, 8.59. IR, ν/cm^{-1}: 3020, 2740, 2500, 2434 (NH, OH); 1700, 1680 (C=O).

Dibenzylammonium 2-formyl-4-nitrophenolate (4). 5-Nitrosalicylaldehyde (1.6 g, 0.01 mol) and dibenzylamine (3 mL) in isopropanol (5 mL) were heated to the boil. The yellow solution obtained was cooled and seeded with crystals of the adduct obtained separately in a test tube by heating a small amount of 5-nitrosalicylaldehyde with piperidine, cooling, and rubbing with a glass stick. The crystals formed were filtered off, washed with toluene and hexane, and dried on a filter. The yield of the product was 2.3 g. When the filtrate was stored, an additional light-yellow crystalline precipitate (~1.5 g) was formed. The total yield was ~3.8 g (quantitative yield), m.p. 79—92 °C (from toluene). Found (%): C, 69.74; H, 5.18; N, 7.29. $C_{21}H_{20}N_2O_4$. Calculated (%): C, 69.23; H, 5.49; N, 7.69. IR, ν/cm^{-1}: 2740, 2454—2327 (NH, OH); 1700 sh, 1681 (C=O); 747, 700 (Ph).

X-ray structural analysis. Crystals of **1** ($C_5H_{12}N^+ \cdot C_7H_4NO_4^-$) are orthorhombic, the space group is $Pna2_1$, at ~20 °C, a = 18.921(9) Å, b = 7.056(3) Å, c = 18.82(1) Å, V = 2513.1(8) Å^3, M = 252.27, Z = 8, μ(Mo-Kα) = 0.10 mm^{-1}, d_{calc} = 1.333 g cm^{-3}. The unit-cell parameters and intensities of 3788 reflections were measured on an automated four-cycle Siemens P3/PC diffractometer (λ(Mo-Kα), graphite monochromator, θ/2θ scanning technique, 2θ < 50°). The structure was solved by the direct method and refined by full-matrix least squares with anisotropic thermal parameters for nonhydrogen atoms. The H atoms were included in the refinement in calculated positions with fixed positional (the riding model) and thermal (U_{iso} = 0.08 Å^2) parameters. The final values of R factors were R = 0.129 and R_w = 0.092 using 1444 independent reflections with $I > 2.5\sigma(I)$. The coordinates for nonhydrogen atoms are given in Table 3. All calculations were performed on an IBM PC/AT-286 computer using the SHELXTL PLUS program package.[9]

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