Molecular Planarity and Crystal Structures of N-Salicylideneaminopyrazine Derivatives

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The crystal structures of N-salicylideneaminopyrazine (SAPz) derivatives, 2SAPz (1) and 3,5-Br-2SAPz (2), were determined by single-crystal X-ray structural analysis. The crystal structures of SAPz derivatives, 2SAPz (1) and 3,5-Br-2SAPz (2), were determined by single-crystal X-ray structural analysis. They were revealed: (1) monoclinic, P2₁/n, a = 4.541(4), b = 19.523(18), c = 10.844(9)Å, β = 97.80(3)°, Z = 4, V = 952.5(15)Å³, R₁ = 0.0651 [I > 2σ(I)]; (2) orthorhombic, P2₁2₁2₁, a = 3.9508(4), b = 10.8449(11), c = 27.627(3)Å, Z = 4, V = 1183.7(2)Å³, R₁ = 0.0494 [I > 2σ(I)]. These molecular conformations are planar because of the lack of intramolecular steric repulsion with the pyrazine ring. The dihedral angles between phenol ring and pyrazine ring were 5.26(11) and 10.0(4)°, respectively.

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Schiff bases (also called azomethines) are considered to be important organic compounds containing acyclic and cyclic imine C=N bonds, which have various applications in photoluminescence materials, optical materials and devices, and color print materials.5

N-Salicylideneaniline (SA), which is one of the Schiff bases, and its structural analogues are known to show photochromism in the crystalline state upon UV light irradiation.6 Interestingly, SA crystals including non-planar molecules with dihedral angle between two aromatic rings greater than 30° are photochromic, and those including planar molecules with a dihedral angle of less than 20° are non-photochromic.7,8 N-Salicylideneaminopyrazine (SAPz) is one of the SA derivatives that include a pyrazine (Pz) (Fig. 1). SAPz derivative molecules would prefer a planar conformation by taking one of two possible Pz orientations, which avoids the intramolecular H to H steric repulsion between Pz C-H and imine C-H. On the other hand, SA derivatives have always suffered from such steric repulsions, so the conformation may not be necessarily planar. In order to demonstrate that SAPz crystals have planar molecules, but no photochromic property, we synthesized two SAPz derivatives of 2SAPz (1) and 3,5-Br-2SAPz (2), and analyzed their crystal structures and photochromic properties.

![Chemical structures of 1 and 2.](image)

The synthesis schemes of compounds 1 and 2 are as follows: A mixture of salicylaldehyde derivative (10 mmol) and 2-aminopyrazine (10 mmol) was heated at 393 K for 2 h without a plug. The resulting melt was cooled, and then red crude title compounds were precipitated. Single crystals were obtained by recrystallizations from chloroform and methanol, respectively.

Single crystals X-ray diffraction data were collected at 293 K on a R-AXIS RAPID imaging plate area detector (RIGAKU) using graphite-monochromated Mo-Kα radiation from a rotating anode source. Scaling and absorption corrections were performed using ABSCOR.9 Crystal data and refinement details of 1 and 2 are given in Table 1. The initial structures were determined by using a dual space method with SHELXTL-2014/4, and refined by full-matrix least-squares on F² with SHELXL-2018/1.10,11 All hydrogen atoms were found in difference Fourier maps; however, they were placed by geometrical calculations and treated using a riding model with isotropic temperature factors. ORTEP drawings are shown in Fig. 2. The hydrogen-bond lengths and angles in the crystal of 1 and 2 are summarized in Tables S1 and S2 (Supporting Information), respectively.

Solid-state diffuse reflectance spectra were measured at 298 K with a JASCO V-560 spectrometer. Analytical samples were prepared as a mixture of the 2SAPz crystals (10 mg) and barium sulfate powder (100 mg). UV irradiation was performed with a high-power UV-LED irradiator (Keyence Corporation) at a wavelength of 365 nm. The measured spectra are shown in Fig. S1 (Supporting Information).

In the crystal structure of 1, an intramolecular hydrogen bond is found between O1 and N1 (2.584(3)Å). However, there are no typical intermolecular interactions that include N atoms of the Pz ring, which can act as a proton acceptor.12,13 The molecules are stacked along the a axis by π-π stacking interactions (Cg-Cg: 4.541(4)Å, Fig. S1). The molecular conformation of 1 is planar with a small dihedral angle between the phenol (C8-N2-C9-C10-C11) and Pz (C1-C2-C3-C4-C5-C6) ring (5.26(11)°). On the other hand, the crystal structure of 2 also shows an intramolecular hydrogen between O1 and N3 (2.587(8)Å), but there are no other typical interactions (Cg-Cg: 4.541(4)Å, Fig. S1).
intermolecular interactions. The crystal structure of \(2\) shows \(\pi\) stacking along the \(a\) axis (Cg-Cg: 3.951(4)\(\AA\), Fig. S2), just the same as \(1\). The molecular conformation of \(2\) is also planar with a small dihedral angle between the phenol (C8-N2-C9-C10-N3-C11) and Pz (C1-C2-C3-C4-C5-C6) ring (10.0(4)\(^\circ\)).

Both SAPz derivatives took a planar molecular conformation in the crystal structures, as expected due to the lack of any steric repulsion between the N atom of the Pz ring and C7-H7 of the azomethine moiety.\(^{14,15}\) Moreover, another SAPz derivative was also reported as having a planar conformation (dihedral angle: 1.25(15)\(^\circ\)), which supports the above consideration.\(^{16}\)

Figure S3 (Supporting Information) shows the diffuse reflectance spectra of \(1\) and \(2\). Because of no spectral change before and after UV irradiation, both compounds are revealed to not show photochromism. These non-photochromic behaviors of \(1\) and \(2\) relate to their planar molecular conformations as well as \(N\)-salicylideneaniline derivatives in which only non-planar molecules show photochromism.\(^{14}\)

In summary, we revealed that the molecular conformations of \(N\)-salicylideneaminopyridine (SAPz) derivatives, \(1\) and \(2\), are planar in the crystal structures due to the absence of any intramolecular steric repulsion. These crystals did not show photochromism because of their planar conformation. The present work provides an idea to lead molecular conformation to be planar by molecular design, which would avoid intramolecular steric repulsion in the crystals.

### Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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**Table 1** Crystal data and refinement details of \(1\) and \(2\)

|       | 1                  | 2                  |
|-------|-------------------|-------------------|
| \(\text{Chemical formula}\) | \(\text{C}_1\text{H}_\text{N}_3\text{O}\) | \(\text{C}_1\text{H}_\text{Br}_2\text{N}_3\text{O}\) |
| \(\text{Formula weight}\)  | 199.21            | 357.02            |
| \(\text{Temperature/K}\) | 293(2)            | 293(2)            |
| \(\text{Wavelength/Å}\)  | 0.71075           | 0.71075           |
| \(\text{Crystal system}\) | monoclinic        | orthorhombic      |
| \(\text{Space group}\)  | \(P2_1/n\)        | \(P2_2_2_2\)      |
| \(a/Å\)                | 4.541(4)          | 3.9508(4)         |
| \(b/Å\)                | 19.523(18)        | 10.844(9)         |
| \(c/Å\)                | 10.844(9)         | 27.627(3)         |
| \(\beta/\)             | 97.80(3)          | 90                |
| \(V/Å^3\)              | 952.5(15)         | 1183.7(2)         |
| \(Z\)                  | 4/1               | 4/1               |
| \(\text{Density/Mg·m}^{-3}\) | 1.389             | 2.003             |
| \(\text{Crystal size/mm}\) | 0.376 × 0.050 × 0.049 | 0.168 × 0.053 × 0.043 |
| \(\text{Reflections collected/unique}\) | 9113/2100 | 11280/2672 |
| \(\theta\) range for data collection/\(^\circ\) | 3.661 to 27.481 | 3.497 to 27.423 |
| \(\text{Completeness to theta} = 25.242\(^\circ\)/\(^\circ\)\) | 99.8%           | 99.6%             |
| \(\text{Data/Restraints/Parameters}\) | 21600/136 | 2672/0/155 |
| \(R\) indices \(I>2\sigma(I)\)/\(R_1\) (\(wR_1\)) | 0.0651 (0.1629) | 0.0494 (0.1111) |
| \(R\) indices \(\text{all data}:/R_1\) (\(wR_1\)) | 0.0990 (0.1888) | 0.0604 (0.175) |
| \(\text{Largest diff. peak and hole/Å}^{-3}\) | 0.359 and –0.259 | 1.865 and –0.528 |
| \(\text{CCDC deposition number}\) | 1848758 | 1848759 |

**Fig. 2** ORTEP drawing of \(1\) and \(2\), showing 50% probability ellipsoids.