Crystal Structure of a Complex between *p*-Nitrophenol and 2-Pyridone

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Molecular recognitions based on weakly interactive forces have attracted considerable interest in recent years, especially in relation to homeostases of lifeforms. Among such recognitions, hydrogen bonding is the most frequently evaluated, since it is indispensable for nucleic acid derivatives to hybridize and function. The key components in hydrogen-bond formations of biomolecules are defined as amide (or lactam) structures. Previously, on the acylation of *p*-nitrophenol with 2-trifluoroacetoxypyridine, we isolated complex **1** instead of obtaining the expected reaction products and found it to be

composed of *p*-nitrophenol and 2-pyridone in a 1:1 ratio.¹ Here, we wish to report the details of the crystal structure of complex **1**.

Solutions of 2-pyridone and *p*-nitrophenol in Et₂O were prepared separately. Equimolar amounts of each were mixed and the mixture was kept for 2 h at room temperature to precipitate crude **1**. The crude **1** was subjected to a slow recrystallization from its dilute solution in Et₂O to give pure **1**. Crystal and experimental data are listed in Table 1. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from a difference Fourier map and included in the final cycle of the full-matrix least-squares refinements. Positional parameters for non-hydrogen atoms are listed in Table 2. The crystal structure of complex **1** is shown in Fig. 1, together with the atomic labeling scheme. Selected intra- and intermolecular bond distances and angles are listed in Table 3. In the crystal structure of 2-pyridone, C=O and N-H groups were linked by hydrogen bonds, the head-to-tail type repetition

Table 1 Crystal structure of molecular complex **1**

Formula: C ₁₁ H ₁₀ N ₂ O ₄
Formula weight = 234.21
Crystal system: monoclinic
Space group: <i>P</i> 2 ₁ / <i>c</i> <i>Z</i> = 4
<i>a</i> = 3.841(1) Å
<i>b</i> = 9.850(4) Å <i>β</i> = 92.20(2)°
<i>c</i> = 28.613(5) Å
<i>V</i> = 1081.7(6) Å ³
<i>D</i> _{calc} = 1.44 g/cm ³
<i>μ</i> (Mo K _α) = 1.04 cm ⁻¹
<i>T</i> = 296 K
Crystal: colorless prism
Crystal size: 0.1 × 0.1 × 0.3 mm
<i>λ</i> (Mo K _α) = 0.71069 Å
2 θ - ω scans with 2 θ _{max} = 120.1°
<i>R</i> = 0.038
<i>R</i> _w = 0.041
Goodness-of-fit = 1.40
(Δ / σ) _{max} = 0.11
($\Delta\rho$) _{max} = 0.13 eÅ ⁻³
($\Delta\rho$) _{min} = -0.15 eÅ ⁻³
No. of reflections measured = 2994
No. of reflections used = 1206 (<i>I</i> > 3 σ (<i>I</i>))
No. of parameters = 194
Measurement: Rigaku AFC-5R
Program system: TEXSAN
Structure determination: direct method (MITHRIL)
Refinement: full-matrix least-squares

Table 2 Fractional coordinates and thermal parameters for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²
O(1)	0.5487(5)	0.1469(2)	0.08492(7)	4.4(1)
O(2)	0.0415(6)	0.2779(2)	0.28436(7)	6.2(1)
O(3)	0.2648(7)	0.0792(2)	0.29606(7)	6.9(1)
O(4)	-0.3592(5)	-0.3568(2)	-0.03152(6)	4.2(1)
N(1)	0.1931(7)	0.1764(3)	0.27055(8)	4.6(1)
N(2)	-0.2605(6)	-0.4025(2)	0.04547(8)	3.6(1)
C(1)	0.3053(7)	0.2747(3)	0.1473(1)	3.5(1)
C(2)	0.4589(6)	0.1589(3)	0.12983(8)	3.3(1)
C(3)	0.5256(7)	0.0489(3)	0.1593(1)	3.5(1)
C(4)	0.4423(7)	0.0551(3)	0.2053(1)	3.6(1)
C(5)	0.2900(7)	0.1714(2)	0.22189(8)	3.3(1)
C(6)	0.2194(7)	0.2813(3)	0.1932(1)	3.6(1)
C(7)	-0.2287(7)	-0.3194(2)	0.00788(9)	3.4(1)
C(8)	-0.0514(8)	-0.1955(3)	0.0168(1)	4.1(1)
C(9)	0.0710(8)	-0.1634(3)	0.0606(1)	4.4(1)
C(10)	0.0224(8)	-0.2522(3)	0.0982(1)	4.3(1)
C(11)	-0.1418(8)	-0.3702(3)	0.0895(1)	3.9(1)

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$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

Fig. 1 Crystal structure of molecular complex 1.

Table 3 Selected intra- and intermolecular bond distances (Å) and angles (°)

Atom	Atom	Distance	Atom	Atom	Distance
O(1)A	O(4)	2.66(3)	N(2)	C(7)	1.361(3)
O(4)	C(7)	1.271(3)	N(2)	O(4')B	2.81(3)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N(2)	C(7)	O(4)	118.8(2)	C(7)	O(4)	H(5)A	113(1)
H(10)	N(2)	C(7)	115(2)	H(5)A	O(4)	H(10')B	116(1)
N(2)	H(10)	O(4')B	173(3)	O(1)A	H(5)A	O(4)	178(3)
C(7)	O(4)	H(10')B	123(1)				

When positions of uncoded atoms are given by (x, y, z), those of coded atoms are as follows: A, (-x, -y, -z); B, (-1-x, -1-y, -z).

of which formed a helical pillar.² On the other hand, in the crystal structure of *p*-nitrophenol, O-H and NO₂ groups were linked by hydrogen bonds, the head-to-tail type repetition of

which formed a linear pillar.³ In contrast, the molecular crystal **1** possesses structural features as follows. The C=O and N-H groups in two units of 2-pyridone are linked to each other by hydrogen bonds [O(4)⋯H(10') and H(10)⋯O(4'), 1.93 Å] to give a cyclic dimer, which is further linked by hydrogen bonds [O(4)⋯H(5) and O(4')⋯H(5'), 1.75 Å] to a hydroxy group of *p*-nitrophenol to constitute a 2:2 complex as a structural unit (Fig. 1). In addition, the cyclic dimer plane and the phenyl ring of *p*-nitrophenol were twisted with the angle of 54.4°.

References

1. T. Keumi, M. Shimada, T. Morita, and H. Kitajima, *Bull. Chem. Soc. Jpn.*, **1990**, 63, 2252.
2. B. R. Penfold, *Acta Cryst.*, **1953**, 6, 591.
3. P. Coppens and G. M. J. Schmidt, *Acta Cryst.*, **1965**, 18, 62.