Crystal Structure of α -(*p*-Methylylamino-*o*-nitrobenzyl)pyridine

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It was found that α -(*p*-butyrylamino-*o*-nitrobenzyl)pyridine (I) (Fig. 1) has an ameliorative effect on learning and memory in various experimental amnesia models of rodents, and increases the contents of monoamines.¹ The title compound (II) (Fig. 1) is one of the derivatives; an X-ray analysis was undertaken in order to determine the inherent conformation and to study the structure-activity relationships.

A pale-yellow prism crystal (0.3×0.2×0.1 mm) was

obtained from an acetone solution at 293(5)K. The crystal and experimental data are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares methods with anisotropic temperature factors for non-H atoms. All H atoms were found from difference Fourier maps and refined isotropically. The atomic parameters for non-hydrogen atoms are listed in Table 2.

Selected bond distances and angles are listed in Table 3. An ORTEP II² drawing of the title compound together with the atomic numbering is shown in Fig. 2. The relative orientation of the pyridine and phenyl

Fig. 1 Chemical structures.

Table 1 Crystal and experimental data

Formula: C ₁₄ H ₁₃ N ₃ O ₃
Formula weight: 271.27
Crystal system: monoclinic
Space group: <i>P</i> 2 ₁ / <i>a</i> <i>Z</i> =4
<i>a</i> =7.430(5)Å
<i>b</i> =23.943(8)Å β =112.61(5)°
<i>c</i> =8.007(4)Å
<i>V</i> =1315(1)Å ³
<i>D_x</i> =1.37 g/cm ³
No. of reflections used=2194
2 θ _{max} =147° with Cu K α
<i>R</i> =0.044
(Δ / σ) _{max} =0.01
($\Delta\rho$) _{max} =0.21 eÅ ⁻³
($\Delta\rho$) _{min} =-0.19 eÅ ⁻³
Measurement: Enraf-Nonius CAD-4 Turbo
Program system: Rigaku teXsan ⁴
Structure determination: SAPI91 ⁵
Refinement: full-matrix

Table 2 Atomic coordinates and equivalent isotropic thermal parameters(*B*_{eq})

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O1	0.6801(3)	0.29190(7)	0.8620(3)	6.53(5)
O2	0.5026(3)	0.34459(7)	0.9519(3)	6.10(5)
O3	0.3037(3)	0.50637(8)	0.6934(3)	6.69(5)
N1	1.1556(3)	0.36756(7)	1.2997(2)	4.12(4)
N2	0.6356(3)	0.33777(7)	0.9006(2)	4.09(4)
N3	0.6085(3)	0.53236(7)	0.7227(3)	3.92(4)
C1	1.0419(4)	0.27418(9)	1.2396(3)	4.54(5)
C2	1.0663(4)	0.2672(1)	1.4172(3)	5.32(6)
C3	1.1357(4)	0.3107(1)	1.5362(4)	5.36(6)
C4	1.1765(4)	0.3600(1)	1.4698(3)	5.07(6)
C5	1.0877(3)	0.32465(7)	1.1830(3)	3.32(4)
C6	1.0686(4)	0.33477(9)	0.9915(3)	3.90(5)
C7	0.9370(3)	0.38370(8)	0.9029(2)	3.19(4)
C8	0.7403(3)	0.38698(7)	0.8758(2)	3.19(4)
C9	0.6283(3)	0.43472(8)	0.8207(3)	3.41(4)
C10	0.7109(3)	0.48183(8)	0.7777(3)	3.36(4)
C11	0.9030(3)	0.47900(9)	0.7918(3)	3.62(4)
C12	1.0122(3)	0.43137(8)	0.8567(3)	3.48(4)
C13	0.4167(3)	0.5422(1)	0.6864(3)	4.26(5)
C14	0.3524(5)	0.6013(1)	0.6349(4)	5.04(6)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

Table 3 Selected bond distances(Å) and angles(°)

O1 --- N2	1.220(2)	O2 --- N2	1.218(2)	O3 --- C13	1.217(3)
N1 --- C4	1.322(3)	N1 --- C5	1.349(2)	N2 --- C8	1.466(2)
N3 --- C10	1.407(3)	N3 --- C13	1.362(3)		
C4 --- N1 --- C5	118.3(2)	O1 --- N2 --- O2	122.7(2)		
O1 --- N2 --- C8	118.6(2)	O2 --- N2 --- C8	118.6(2)		
C10 --- N3 --- C13	127.8(2)	N1 --- C4 --- C3	124.0(2)		
N1 --- C5 --- C1	120.9(2)	N1 --- C5 --- C6	116.6(2)		
N2 --- C8 --- C7	120.8(2)	N2 --- C8 --- C9	115.0(2)		
N3 --- C10 --- C9	122.6(2)	N3 --- C10 --- C11	118.9(2)		
O3 --- C13 --- N3	123.4(2)	O3 --- C13 --- C14	121.7(2)		
N3 --- C13 --- C14	114.8(2)				

rings is different from that of (I).³ The two rings are almost perpendicular to each other. The dihedral angle between the least-squares planes of the rings is 88.5(3)°, which is 88.8(5)° in (I). The torsion angles of N1-C5-C6-C7 and C5-C6-C7-C12 in (II) are -57.9(3) and -113.6(2)°, respectively. In (I) they are -20.5(2) and -81.9(2)°, respectively. The nitro group is markedly twisted out of the phenyl ring [O1-N2-C8-C7 33.8(3)°]. The magnitude of the torsion angle is significantly larger than that of 20.3(2)° in (I). In the present compound the amide group is slightly twisted out of the phenyl ring [C9-C10-N3-C13 6.7(3)°, O3-C13-N3-C10 1.9(4)°]. The amide group, however, is considerably rotated from coplanarity with the phenyl ring in (I) [C9-C10-N3-C13 140.8(1)°]. The bond distances and angles in the molecule are within the normal ranges. There is an intermolecular hydrogen bond between the nitrogen atoms in the amide group and the pyridine ring [N1...N3 (2-x, 1-y, 2-z)=3.014(3)Å, ∠N1...H-N3=177(2)°].

Fig. 2 ORTEP drawing of the molecule, representing heavy atoms as 50% probability ellipsoids and H atoms as spheres of arbitrary radius.

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