

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE AND DFT STUDY OF *N*-PHENYL-*N*-(PYRIDIN-4-YL)ACETAMIDE

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The title compound *N*-phenyl-*N*-(pyridin-4-yl)acetamide (**1**) crystallizes in the monoclinic crystal system in the space group $P2_1/n$ with unit cell parameters $a = 9.097(7) \text{ \AA}$, $b = 11.824(11) \text{ \AA}$, $c = 10.128(10) \text{ \AA}$, $\beta = 106.64(2)^\circ$, $V = 1043.8(16) \text{ \AA}^3$ and $Z = 4$. The structure of the amide unit is almost planar. The dihedral angles of the amide plane with the benzene and pyridine rings are $58.40(5)^\circ$ and $61.51(5)^\circ$ respectively, indicating that neither phenyl nor pyridyl group is conjugated with the amide unit.

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The conformation of the carbonyl group in *N,N*-diarylamides has received interest due to their reactivities [1]. The conformation where the oxygen atom of the carbonyl group has a close contact with an electron-deficient aryl group is considered to be favorable because of the effective conjugation and an intramolecular hydrogen bond with the aryl group. We report the structure and DFT study of *N*-phenyl-*N*-(pyridin-4-yl)acetamide (**1**) where a phenyl group of diphenylacetamide is replaced by the pyridyl group.

Experimental. The preparation of **1** was carried out according to the literature [2, 3]. The single crystals were obtained by recrystallization from dichloromethane. X-ray data from a monoclinic crystal (colorless block, $0.10 \times 0.05 \times 0.05 \text{ mm}$) were collected on a RIGAKU Saturn 724+ CCD device at 93 K. Crystallographic parameters are as follows: space group $P2_1/n$, $a = 9.097(7) \text{ \AA}$, $b = 11.824(11) \text{ \AA}$, $c = 10.128(10) \text{ \AA}$, $\beta = 106.64(2)^\circ$, $V = 1043.8(16) \text{ \AA}^3$, $Z = 4$, empirical formula $C_{13}H_{12}N_2O$, $M = 212.25$, $d_x = 1.351 \text{ g/cm}^{-3}$, $F(000) = 448.00$. The intensities of 7652 reflections (multi-layered mirror monochromatic MoK_α radiation, $2\theta_{\max} = 52^\circ$, $R_{\text{int}} = 0.0418$ for 2027 unique reflections (1652 for $I > 2\sigma(I)$), numerical absorption correction) were measured; $R(I > 2\sigma(I), \text{ all data}) = 0.0425$, 0.0567 , $wR(I > 2\sigma(I), \text{ all data}) = 0.0926$, 0.0996 , GOOF on $F^2 = 1.050$, $\Delta\rho_{\max} = 0.23 \text{ e/\AA}^{-3}$, $\Delta\rho_{\min} = -0.23 \text{ e/\AA}^{-3}$, Data / restraints / parameters = 2027 / 0 / 146.

The structure was solved by a direct method (SHELXD) [4] and was refined by the full-matrix least squares method (SHELXL97) [5]. The positions of the C-bound H atoms were obtained by the calculation and were refined as riding on their parent C atoms. $U_{\text{iso}}(\text{H})$ values of the H atoms were set at $1.2U_{\text{eq}}$ (parent atom for C). CIF-file containing complete information on studied structure was deposited with CCDC 940755, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The crystal structure of **1** is shown in Fig. 1, *a*. The structure of the C1/C7/N1/C12/O1/C13 amide unit is almost planar (r.m.s. deviation = 0.0278 \AA). The dihedral angles of the amide plane with the benzene and pyridine rings are $58.40(5)^\circ$ and $61.51(5)^\circ$ respectively, indi-

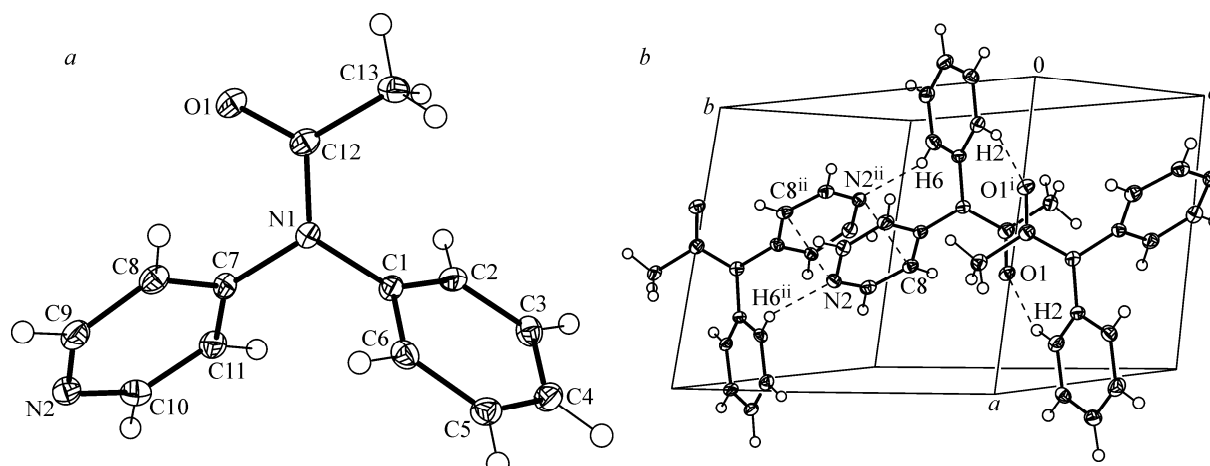


Fig. 1. Crystal structure of **1** (a) and the crystal packing structure of the asymmetric unit (b). Intermolecular contacts: C2—H2 \cdots O1ⁱ = 2.460(2) Å, C6—H6 \cdots N2ⁱⁱ = 2.599(2) Å, N2 \cdots C8ⁱⁱ = 3.460(3) Å (symmetry codes: (i) 1-x, -y, -z, (ii) 1-x, 1-y, -z). Plane-plane and centroid—centroid distances of the pyridine rings: 3.3393(6) Å and 3.945(4) Å

cating that neither phenyl nor pyridyl group is well conjugated with the amide unit. The oxygen atom of the carbonyl group has the same side with the pyridyl ring, but intramolecular hydrogen bonds cannot be recognized. There are five kinds of intermolecular contacts: C2—H2 \cdots O1ⁱ hydrogen bonds, C6—H6 \cdots N2ⁱⁱ hydrogen bonds, and the $\pi\cdots\pi$ stacking interaction, as shown in Fig. 1, b. The remaining two weak C—H \cdots π interactions are detected as C4—H4 \cdots π (N2/C7—C10 pyridyl)ⁱⁱⁱ and C10—H10 \cdots π (C1—C6 phenyl)^{iv} (symmetry codes: (iii) x-1, y, z, (iv) x+1/2, -y+1/2, -z-1/2), whose geometries are 2.81 Å and 2.77 Å for H4 \cdots center and H4 \cdots plane, and 2.91 Å and 2.86 Å for H10 \cdots center and H4 \cdots plane.

DFT calculations converged to two stable conformers (I and II), depending on the direction of the carbonyl group as shown in Fig. 2. Conformer I was estimated to be more stable than conformer II by 7.4 kJ·mol⁻¹, and the energy difference indicated little population of conformer II at room temperature. In conformer I, the pyridyl group has a smaller angle (ca 25.4°) with the amide plane, although the phenyl group has a larger angle (ca 75.6°) with the plane. The smaller dihedral angle of the pyridyl ring is thought to originate in the intramolecular C—H \cdots O hydrogen bond and also in the effective conjugation between the nitrogen lone pair and the ring.

In diarylacetamide derivatives, the dihedral angles of the aryl groups with the amide plane indicate a tendency that the relatively electron-deficient ring has a smaller angle [1, 8, 9]. However, in **1**, the electron-deficient pyridyl ring still has a relatively large dihedral angle which differs from that

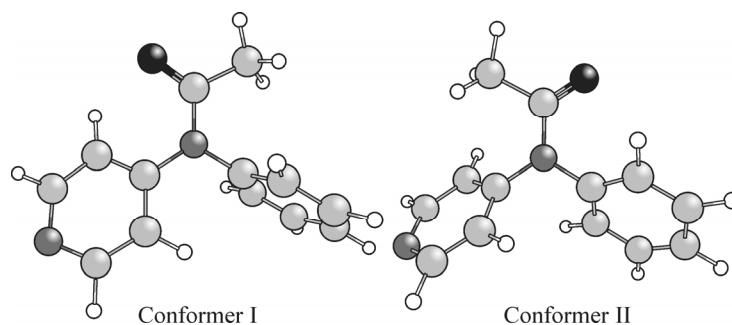


Fig. 2. Two stable conformers of **1** obtained by DFT calculations (GAMESS) at the B3LYP 6-31G(d) level. [6, 7]

in the related or optimized structures. This is presumably because the intermolecular hydrogen bonds, the $\pi \cdots \pi$ stacking interaction, and the C—H $\cdots\pi$ interactions stabilize the crystal more effectively.

Conclusions. We have succeeded in the crystal structure determination of **1**. The structure is not very different from that of the related or optimized structures, because the orientation of the C=O group is the same, namely the carbonyl oxygen atom is close to an electron-deficient ring as in literature and calculated structures. Only the interrelation of the dihedral angles of the amide plane with the benzene and pyridine rings is different. The reason for a such thing cannot be explained only by the intermolecular hydrogen bonds and the $\pi \cdots \pi$ stacking interaction because there are similar interactions in the referred structures of *N*-(4-nitrophenyl)-*N*-phenylacetamide from [8] and *N*-(4-methoxyphenyl)-*N*-(4-nitrophenyl)acetamide from [9]. This problem is very complicated and the most plausible reason lies in the interplay of intermolecular interactions and the close-packing principle.

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REFERENCES

1. Yamasaki R., Tanatani A., Azumaya I., Saito S., Yamaguchi K., Kagechika H. // *Org. Lett.* – 2003. – **5**, N 8. – P. 1265 – 1267.
2. Petrow V. // *J. Chem. Soc.* – 1945. – P. 927 – 928.
3. Zee S., Wang W. // *J. Chin. Chem. Soc.* – 1980. – **27**. – P. 147 – 149.
4. Schneider T.R., Sheldrick G.M. // *Acta Crystallogr.* – 2002. – **D58**. – P. 1772 – 1779.
5. Sheldrick G.M. // *Acta Crystallogr.* – 2008. – **A64**. – P. 112 – 122.
6. Schmidt M.W., Baldrige K.K., Boatz J.A., Elbert S.T., Gordon M.S., Jensen J.H., Koseki S., Matsunaga N., Nguyen K.A., Su S., Windus T.L., Dupuis M., Montgomery J.A. // *J. Comput. Chem.* – 1993. – **14**. – P. 1347.
7. Gordon M.S., Schmidt M.W. *Theory and Applications of Computational Chemistry: the first forty years.* – Amsterdam: Elsevier, 2005.
8. Kim S.Y., An G., Rhee H. // *Synlett.* – 2003. – N 1. – P. 112 – 114.
9. Krigbaum W.R., Roe R.-J., Woods J.D. // *Acta Crystallogr.* – 1968. – **B24**. – P. 1304 – 1312.