

Victor B. Rybakov,* Alexander A. Tsisevich, Kirill V. Nikitin, Vadim L. Alifanov and Eugene V. Babaev

Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation

Correspondence e-mail: rybakov20021@yandex.ru

Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.054
 wR factor = 0.161
 Data-to-parameter ratio = 15.0

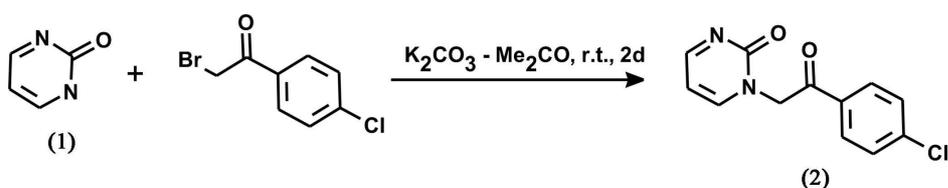
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1-(4-Chlorobenzoylmethyl)pyrimidin-2(1H)-one

The title compound, $\text{C}_{12}\text{H}_9\text{ClN}_2\text{O}_2$, was synthesized and characterized by ^1H NMR and IR spectroscopy and X-ray diffraction techniques. The chlorobenzoyl fragment in the structure is almost flat, whereas the carbonyl group is almost perpendicular to the pyrimidine ring plane.

Comment

We have previously described the crystal structures of a series of *N*-phenacyl-2-pyridones (Albov *et al.*, 2004*a,b*, 2005). We report here the synthesis and crystal structure of their aza-analog, (2). In contrast to well investigated reactions of pyridones with α -halogenoketones, analogous reactions for pyrimidones have been little studied. There are only a few examples, namely the reaction of (1) with the acetal of α -bromoacetaldehyde (Holy *et al.*, 1984) or with chloroacetic acid derivatives (Gefenas & Vainilavichus, 2003) and phenacylation of the 5-chloro derivative of (1) (Benneche & Gandersen, 1988). In all of these cases, the products of *N*-alkylation were exclusively observed. Interestingly, in the study of the phenacylation of sterically hindered 4,6-dimethylpyrimidone, only the *N*-isomers have been isolated (Ivanov *et al.*, 1983; Buchan *et al.*, 1978). Usually these reactions are performed in aprotic bipolar solvents in the presence of bases, so that the alkylated species has been the pyrimidone anion.



We have found that reaction of (1) with *p*-chlorophenacyl bromide in the presence of K_2CO_3 in acetone yields the title compound, (2). The ^1H NMR spectra were useless for distinguishing between *O*- and *N*-isomers. In the IR spectrum of (2), two $\text{C}=\text{O}$ peaks were observed, one for the $-\text{N}-\text{C}=\text{O}$ fragment of pyrimidone and another for the carbonyl group, thus clearly confirming selective *N*-alkylation (in the case of *O*-phenacylation no amide peak would be observed). The structure of the *N*-isomer was finally confirmed by X-ray crystallographic analysis.

In the pyrimidone ring of (2), the single and double bonds alternate (Table 1), though allowing some degree of conjugation. In the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002), we found only one structure with the pyrimidone (2) fragment, namely the parent pyrimidone (1) (Furberg & Solbakk, 1970) with the same distribution of bond lengths. In the structure of (2), the dihedral angle between the

Received 24 April 2006
 Accepted 22 May 2006

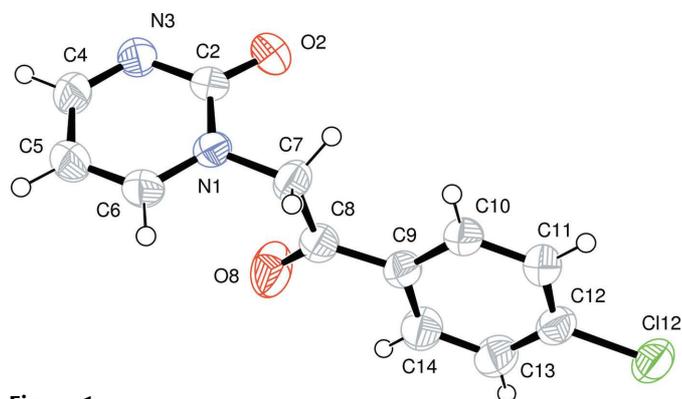


Figure 1

The structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, with H atoms shown as spheres of arbitrary radius.

pyrimidone ring and the C7/C8/O8/C9 unit is $81.57(8)^\circ$. The O8—C8—C9—C14 torsion angle of $-4.2(2)^\circ$ indicates conjugation in the benzoyl fragment.

Experimental

The hydrochloride of (1) (26.5 g; 0.2 mol) was suspended in 500 ml of dry acetone. A solution of 0.1 mol of *p*-chlorophenacyl bromide in 100 ml acetone and 0.4 mol K_2CO_3 was added with stirring. The reaction mixture was stirred for 2 d at room temperature, and then the solvent was evaporated under vacuum. The residue was washed with water and then with ethyl acetate. The product was isolated by suction and recrystallized from acetonitrile. (yield 95%, m.p. 497–499 K). 1H NMR (DMSO- d_6 /TMS): δ J(Hz) 8.57 (*m*, 1H, H-6), 8.02–8.16 (*m*, 3H, 2H of *p*-ClPh, H-4), 7.57 (*m*, 2H, *p*-ClPh), 6.42 (*m*, 1H, H-5), 5.44 (*s*, 2H, NCH₂). IR (nujol) ν_{CO} , cm^{-1} 1695, 1615. Analysis calculated for $C_{12}H_9ClN_2O_2$: C 57.96, H 3.65, N 11.27%; found: C 57.67, H 3.41, N 11.29%.

Crystal data

$C_{12}H_9ClN_2O_2$
 $M_r = 248.66$
 Monoclinic, $P2_1/n$
 $a = 10.2191(10) \text{ \AA}$
 $b = 10.8421(14) \text{ \AA}$
 $c = 11.3449(15) \text{ \AA}$
 $\beta = 115.065(11)^\circ$
 $V = 1138.6(3) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.451 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation
 $\mu = 2.91 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism, colourless
 $0.2 \times 0.2 \times 0.2 \text{ mm}$

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω scans
 Absorption correction: none
 2327 measured reflections
 2327 independent reflections

1842 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 77.9^\circ$
 1 standard reflection
 frequency: 120 min
 intensity decay: 5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.161$
 $S = 1.14$
 2327 reflections
 155 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0895P)^2 + 0.2167P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.79 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0192 (19)

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C6	1.353 (3)	C8—O8	1.213 (3)
N1—C2	1.399 (3)	C8—C9	1.477 (3)
N1—C7	1.455 (3)	C9—C10	1.395 (3)
C2—O2	1.226 (3)	C9—C14	1.396 (3)
C2—N3	1.364 (3)	C10—C11	1.382 (3)
N3—C4	1.307 (3)	C11—C12	1.379 (3)
C4—C5	1.397 (3)	C12—C13	1.384 (4)
C5—C6	1.341 (4)	C12—C12	1.742 (2)
C7—C8	1.514 (3)	C13—C14	1.371 (4)
C6—N1—C2	121.49 (19)	O8—C8—C7	119.5 (2)
C6—N1—C7	120.52 (19)	C9—C8—C7	118.47 (19)
C2—N1—C7	117.84 (19)	C10—C9—C14	118.8 (2)
O2—C2—N3	122.8 (2)	C10—C9—C8	122.9 (2)
O2—C2—N1	119.7 (2)	C14—C9—C8	118.3 (2)
N3—C2—N1	117.53 (19)	C11—C10—C9	120.3 (2)
C4—N3—C2	119.42 (19)	C12—C11—C10	119.4 (2)
N3—C4—C5	124.3 (2)	C11—C12—C13	121.4 (2)
C6—C5—C4	116.6 (2)	C11—C12—C12	119.3 (2)
C5—C6—N1	120.5 (2)	C13—C12—C12	119.22 (19)
N1—C7—C8	111.92 (19)	C14—C13—C12	118.8 (2)
O8—C8—C9	122.0 (2)	C13—C14—C9	121.3 (2)

All H atoms were refined using a riding model, with C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms C—H = 0.97 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH₂ H atoms, and C—H = 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₃ H atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are indebted to the Russian Foundation for Basic Research for covering the licence fee to use the CSD.

References

- Albov, D. V., Rybakov, V. B., Babaev, E. V. & Aslanov, L. A. (2004a). *Acta Cryst. E* **60**, o1098–o1099.
- Albov, D. V., Rybakov, V. B., Babaev, E. V. & Aslanov, L. A. (2004b). *Acta Cryst. E* **60**, o1952–o1953.
- Albov, D. V., Rybakov, V. B., Babaev, E. V. & Aslanov, L. A. (2005). *Cryst. Rep.* **50**, 660–664.
- Allen, H. F. (2002). *Acta Cryst. B* **58**, 380–388.
- Benneche, T. & Gandersen, L. (1988). *Acta. Chem. Scand. Ser. B*, **42**, 384–389.
- Buchan, R., Frazer, M. & Shand, C. (1978). *J. Org. Chem.* **43**, 3544–3547.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Furberg, S. & Solbakk, J. (1970). *Acta Chem. Scand.* **24**, 3230–3236.
- Gefenas, V. I. & Vainilavichus, V. I. (2003). *Chim. Geterotsikl. Soedin.* **20**, 1429–1430. (In Russian.)
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Holy, A., Ludzisa, A. & Votruba, I. (1984). *Coll. Czech. Chem. Commun.* **50**, 393–415.
- Ivanov, V. B., Reznik, V. S. & Efremov, Yu. Ya. (1983). *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)*, **32**, 2130–2134.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.