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CRYSTAL STRUCTURE OF 6-CHLORO-4-NITRO-2-PHENYLPYRIMIDINE

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The crystal structures of 6-chloro-4-nitro-2-phenylpyrimidine and 6-chloro-2-phenylpyrimidine have been determined using X-ray diffraction. The effect of the nitro group and the endocyclic nitrogen atoms on the geometric parameters of the 2- and 4-nitropyrimidine molecules, and also related α-nitroazines are compared.

Keywords: nitropyrimidine, chloropyrimidine, crystal structure.

Earlier we published data on the crystal structure of 2-nitropyridine (**1**) [1], 4,6-dimethyl-2-nitropyrimidine (**2**), and 2-nitro-5-phenylpyrimidine (**3**) [2]. In continuing studies of the geometry of α-nitroazines, we have turned to substituted 4-nitropyrimidines. According to data in the Cambridge Structural Database (CSD) [3], the geometry of this group of compounds has not been studied.

In this paper, using X-ray diffraction we have determined the crystal structure of 6-chloro-4-nitro-2-phenylpyrimidine (**4**) (Tables 1 and 2). For a more correct determination of the effect of the nitro group on the geometric parameters of the pyrimidine ring, we determined the crystal structure of 6-chloro-2-phenylpyrimidine (**5**) (Tables 1 and 3). The geometric characteristics of the indicated compounds (bond lengths and bond angles) are given in Tables 4 and 5.

In compound **4** (Fig. 1) the nitro group is rotated by 14.2(1)° relative to the plane of the pyrimidine ring, while between the planes of the heterocycle and the phenyl ring there is a small dihedral angle of 6.9(1)°. That angle in compound **5** (Fig. 2) is equal to 1.9(1)°. For substituted 2-phenylpyrimidines, the analogous parameter is significantly smaller than for substituted 5-phenylpyrimidines [2,4].

Comparison of the bond lengths in compounds **4** and **5** (see Table 4) shows that when the NO_2 group is introduced into the position 4 of the pyrimidine ring, the endocyclic $N_{(3)}–C_{(4)}$ bond is shortened by 0.023(6) Å and the other bonds remain practically the same, including the endocyclic $C_{(4)}–C_{(5)}$ bond. The $C_{(6)}–Cl$ bond is shortened by 0.012(6) Å.

The change in the endocyclic bonds at the *ipso* carbon atom bonded to the nitro group in compound **4** is similar to the changes observed earlier for other α-nitroazines. So compared with the mean statistical values (Table 6), the endocyclic C–N bond at the *ipso* carbon atom is shortened by 0.029 Å, 0.021 Å, and 0.026 Å respectively for 2-nitropyridines, 2-nitro- and 4-nitropyrimidines. The endocyclic C–C bond is shortened to a lesser extent: by 0.011 Å (2-nitropyridines) and 0.019 Å (4-nitropyrimidine).

For α-nitroazines, typically we see appreciable lengthening of the exocyclic C–N bond (the C–NO_2 bond) by 0.029 Å (2-nitropyridines), 0.034 Å (2-nitropyrimidines), and 0.040 Å (4-nitropyrimidine). The endocyclic C–C bonds at the *ipso* carbon atom in β-nitroazines remain practically the same as the mean

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TABLE 1. Crystallographic Data for Compounds **4** and **5**

Characteristics	Compound **4**	Compound **5**
Empirical formula	$C_{10}H_6ClN_3O_2$	$C_{10}H_7ClN_2$
Molecular weight	235.63	190.63
Type of cell	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
Cell parameters, (Å)	a = 6.3434(9)	a = 6.179(2)
	b = 11.120(2)	b = 7.531(2)
	c = 14.770(2)	c = 10.102(2)
		β = 91.07(2)
	β = 95.45(1)°	β = 101.58(2)
		γ = 98.64(2)
Cell volume (Å^3)	1037.1(3)	451.4(2)
Z	4	2
Crystal dimensions (mm^3)	1.15 × 0.20 × 0.15	1.00 × 0.40 × 0.15
Scanning method	2θ/θ	2θ/θ
θ range (°)	4-70	4-70
Number of reflections	2314	1939
Independent	1969	1710
Correction for absorption	face-indexed	face-indexed
Transmission	0.663-0.309	0.625-0.192
R-factors		
R_1 ($I > 2\sigma$)	0.0512	0.0429
wR_2 (all I)	0.1618	0.1313
S	1.081	1.047
Extinction	0.004(1)	0.050(6)

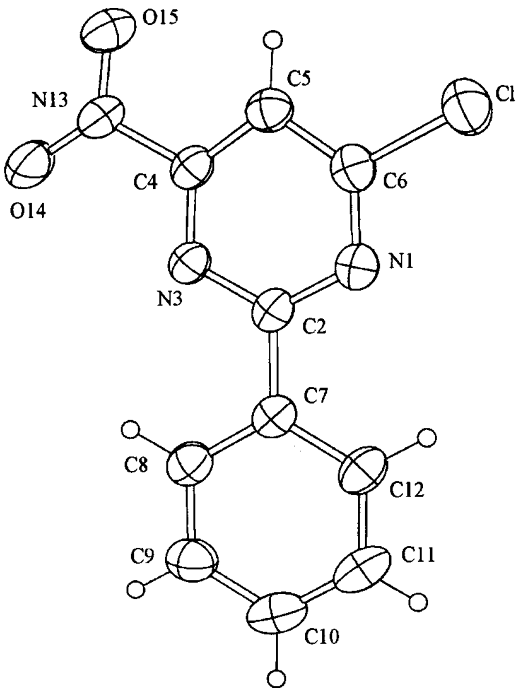

Fig. 1. Structure of the 6-chloro-4-nitro-2-phenylpyrimidine (**4**) molecule according to X-ray diffraction data (25% probability thermal ellipsoids are shown).

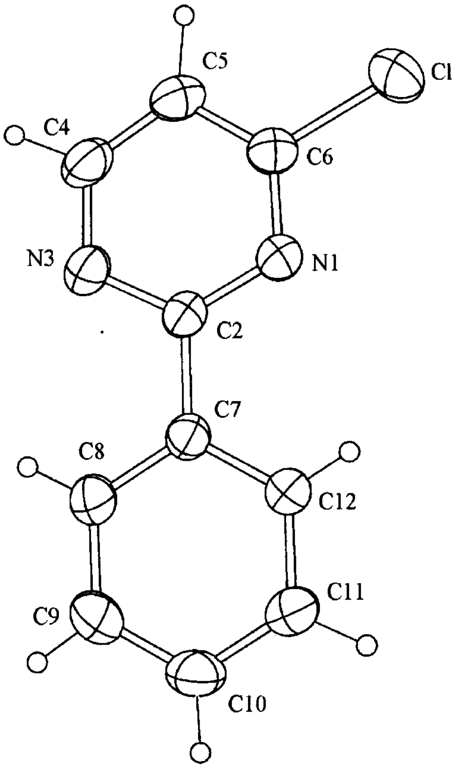

Fig. 2. Structure of the 6-chloro-2-phenylpyrimidine (**5**) molecule according to X-ray diffraction data (25% probability thermal ellipsoids are shown).

statistical values: they are 0.005 Å and 0.006 Å respectively for substituted 3(5)-nitropyridines and 5-nitropyrimidines. The exocyclic C–NO_2 bond is shortened by 0.020 Å for 3(5)-nitropyridines, and does not change for 5-nitropyrimidines (Table 6).

TABLE 2. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Thermal Factors ($Å^2\times10^3$) of Non-hydrogen Atoms for 6-Chloro-4-nitro-2-phenylpyrimidine (**4**)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
$N_{(1)}$	7675(3)	-99(2)	8179(1)	58(1)
$C_{(2)}$	9596(4)	45(2)	8629(2)	52(1)
$N_{(3)}$	10604(3)	1107(2)	8749(1)	54(1)
$C_{(4)}$	9545(4)	2033(2)	8389(2)	55(1)
$C_{(5)}$	7592(4)	2020(2)	7913(2)	61(1)
$C_{(6)}$	6748(4)	872(2)	7827(2)	59(1)
$C_{(7)}$	10705(4)	-1037(2)	9007(2)	54(1)
$C_{(8)}$	12787(5)	-965(3)	9390(2)	66(1)
$C_{(9)}$	13821(6)	-1977(3)	9739(2)	77(1)
$C_{(10)}$	12788(6)	-3073(3)	9708(2)	80(1)
$C_{(11)}$	10740(7)	-3148(3)	9328(2)	79(1)
$C_{(12)}$	9671(5)	-2142(2)	8979(2)	67(1)
$N_{(13)}$	10673(4)	3220(2)	8532(2)	66(1)
$O_{(14)}$	12505(4)	3212(2)	8788(2)	103(1)
$O_{(15)}$	9604(4)	4110(2)	8370(2)	85(1)
Cl	4312(1)	662(1)	7215(1)	83(1)

TABLE 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Factors ($Å^2 \times 10^3$) of Non-hydrogen Atoms for 6-Chloro-2-phenylpyrimidine (**5**)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
$N_{(1)}$	1512(2)	2233(2)	1562(2)	59(1)
$C_{(2)}$	-229(3)	2175(2)	485(2)	53(1)
$N_{(3)}$	-2391(2)	1577(2)	480(2)	67(1)
$C_{(4)}$	-2778(3)	1030(3)	1667(2)	74(1)
$C_{(5)}$	-1121(4)	1048(3)	2831(2)	71(1)
$C_{(6)}$	1022(3)	1672(3)	2693(2)	63(1)
$C_{(7)}$	244(3)	2823(2)	-811(2)	53(1)
$C_{(8)}$	-1480(3)	2782(3)	-1969(2)	70(1)
$C_{(9)}$	-1035(4)	3408(3)	-3173(2)	84(1)
$C_{(10)}$	1128(4)	4082(3)	-3228(2)	77(1)
$C_{(11)}$	2858(4)	4123(3)	-2096(2)	75(1)
$C_{(12)}$	2427(3)	3487(3)	-888(2)	66(1)
Cl	3288(1)	1726(1)	4097(1)	99(1)

RHF/6-31G* calculations for compounds **4** and **5** (Tables 4 and 5) agree with experimental data, and also indicate that when a nitro group is introduced, the endocyclic bonds $C_{(4)}–N_{(3)}$ and $C_{(4)}–C_{(5)}$ at the *ipso* carbon atom are shortened by respectively 0.020 Å and 0.008 Å (Table 4).

Comparison of the geometric parameters of compounds **4** and **5** using X-ray diffraction data shows that introducing an NO_2 group leads to an increase in the intracyclic bond angle at the *ipso* $C_{(4)}$ atom by 3.5°, and a decrease in the angles at the vicinal atoms by 1.2° at $N_{(3)}$ and by 2.3° at $C_{(5)}$.

The remaining angles in the molecule do not change. This is consistent with our observations that introducing a nitro group in the α position relative to the nitrogen atom of the azine ring leads to an increase in the intracyclic bond angle at the *ipso* carbon atom by ~3° [2]. According to the calculations, the increase in the $N_{(3)}–C_{(4)}–C_{(5)}$ angle is 2.4° when an NO_2 group is introduced into compound **5** (Table 5).

TABLE 4. Bond Lengths (Å) in the Molecules of Compounds **4** and **5**

Bond lengths	6-Chloro-4-nitro-2-phenylpyrimidine **4**		6-Chloro-2-phenylpyrimidine **5**	
	ab initio	X-ray diffraction	*ab initio*	X-ray diffraction
$N_{(1)}–C_{(2)}$	1.331	1.341(3)	1.330	1.336(2)
$C_{(2)}–N_{(3)}$	1.323	1.347(3)	1.322	1.343(2)
$N_{(3)}–C_{(4)}$	1.299	1.313(3)	1.319	1.336(3)
$C_{(4)}–C_{(5)}$	1.371	1.365(4)	1.379	1.367(3)
$C_{(5)}–C_{(6)}$	1.390	1.385(3)	1.383	1.376(3)
$C_{(6)}–N_{(1)}$	1.300	1.314(3)	1.301	1.310(2)
$C_{(4)}–N_{(13)}$	1.482	1.508(3)	—	—
$N_{(13)}–O_{(14)}$	1.182	1.187(3)	—	—
$N_{(13)}–O_{(15)}$	1.195	1.210(3)	—	—
$C_{(2)}–C_{(7)}$	1.480	1.476(3)	1.485	1.482(2)
$C_{(7)}–C_{(8)}$	1.393	1.388(4)	1.392	1.384(2)
$C_{(8)}–C_{(9)}$	1.383	1.378(4)	1.384	1.383(3)
$C_{(9)}–C_{(10)}$	1.386	1.382(4)	1.386	1.371(3)
$C_{(10)}–C_{(11)}$	1.386	1.368(5)	1.386	1.369(3)
$C_{(11)}–C_{(12)}$	1.383	1.382(4)	1.384	1.386(3)
$C_{(12)}–C_{(7)}$	1.392	1.391(3)	1.392	1.387(2)
$C_{(6)}–Cl$	1.727	1.730(3)	1.735	1.742(2)

TABLE 5. Bond Angles (deg.) in Molecules of Compounds **4** and **5**

Angle	6-Chloro-4-nitro-2-phenylpyrimidine **4**		6-Chloro-2-phenylpyrimidine **5**	
	ab initio	X-ray diffraction	*ab initio*	X-ray diffraction
$N_{(1)}$–$C_{(2)}$–$N_{(3)}$	123.5	124.6(2)	124.4	125.2(2)
$C_{(2)}$–$N_{(3)}$–$C_{(4)}$	116.8	114.6(2)	117.3	115.8(2)
$N_{(3)}$–$C_{(4)}$–$C_{(5)}$	125.5	127.2(2)	123.1	123.7(2)
$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	112.6	112.4(2)	114.4	114.7(2)
$C_{(5)}$–$C_{(6)}$–$N_{(1)}$	123.7	124.5(2)	123.6	124.7(2)
$C_{(6)}$–$N_{(1)}$–$C_{(2)}$	117.8	116.7(2)	117.3	116.0(2)
$N_{(3)}$–$C_{(4)}$–$N_{(13)}$	115.9	114.3(2)	—	—
$C_{(5)}$–$C_{(4)}$–$N_{(13)}$	118.6	118.5(2)	—	—
$C_{(4)}$–$N_{(13)}$–$O_{(14)}$	117.9	118.4(2)	—	—
$C_{(4)}$–$N_{(13)}$–$O_{(15)}$	115.9	116.0(2)	—	—
$O_{(14)}$–$N_{(13)}$–$O_{(15)}$	126.2	125.6(2)	—	—
$N_{(1)}$–$C_{(2)}$–$C_{(7)}$	118.2	117.9(2)	117.4	117.8(1)
$N_{(3)}$–$C_{(2)}$–$C_{(7)}$	118.2	117.5(2)	118.2	117.0(2)
$C_{(2)}$–$C_{(7)}$–$C_{(8)}$	120.1	120.5(2)	120.2	120.8(2)
$C_{(2)}$–$C_{(7)}$–$C_{(12)}$	120.4	120.1(2)	120.5	120.7(2)
$C_{(8)}$–$C_{(7)}$–$C_{(12)}$	119.6	119.4(2)	119.3	118.5(2)
$C_{(7)}$–$C_{(8)}$–$C_{(9)}$	120.1	120.4(3)	120.3	120.7(2)
$C_{(8)}$–$C_{(9)}$–$C_{(10)}$	120.1	120.0(3)	120.1	120.1(2)
$C_{(9)}$–$C_{(10)}$–$C_{(11)}$	120.1	119.7(3)	119.9	120.1(2)
$C_{(10)}$–$C_{(11)}$–$C_{(12)}$	120.1	121.1(3)	120.1	120.1(2)
$C_{(11)}$–$C_{(12)}$–$C_{(7)}$	120.1	119.4(3)	120.3	120.5(2)
$N_{(1)}$–$C_{(6)}$–Cl	117.3	116.1(2)	117.0	116.2(1)
$C_{(5)}$–$C_{(6)}$–Cl	119.0	119.4(2)	119.4	119.1(2)

In contrast to previously studied α-nitroazines **1-3**, in the 4-nitropyrimidine **4**, according to X-ray diffraction we observe asymmetry in the nitro group: one N–O bond is 0.023 Å longer than the other (Table 4). The calculations for compound **4** (Table 4) also suggest that the N–O bonds are different by 0.013 Å. Asymmetry in the nitro group in α-nitroazines was predicted by 3-21G* calculations for unsubstituted 4-nitropyrimidine and 2-nitropyridine **1** [7]. But it has been experimentally demonstrated (by X-ray diffraction) that in the crystal phase, for 2-nitropyridine these bonds are practically identical: they are only 0.004 Å different [1].

TABLE 6. Average C–C and C–N Bond Lengths at the *ipso* Carbon Atom of Substituted Nitropyridines and Nitropyrimidines

Bond	Mean statistical values [5]	α-Nitroazines			β-Nitroazines	
		2-nitro-pyridines [2]	2-nitro-pyrimidines [2]	4-nitro-pyrimidine **4**	3-nitro-pyridines*	2-R-5-nitro-pyrimidines [6]*2
N–C–N_{Pym}	1.333(13)	—	1.312(2)	—	—	—
N–C_{Pym}	1.339(15)	—	—	1.313(3)		—
N–C_{Py}	1.337(12)	1.308(6)	—	—		—
C–C_{Ar}	1.384(13)	1.373(16)	—	1.365(4)	1.381(6)	1.378(11)
C_{Ar}–NO_2	1.468(14)	1.497(6)	1.502(4)	1.508(3)	1.448(12)	1.468(1)

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* Using 9 structures of substituted 3-nitropyridines, taken from the Cambridge Structural Database [3], with σ_f = 1 and without substituents *ortho* to the nitro group.

*2 Without substituents at the 4, 6 positions.

Note the slightly shortened intermolecular Cl···O contact of 3.080(2) Å in the crystal of compound **4** compared with the sum of the van der Waals radii, 3.13 Å [8].

The data obtained in this work support hypotheses that the nitro group in substituted α-azine molecules has the same kind of effect on redistribution of *s*- and *p*-electrons in formation of endocyclic and exocyclic C–N bonds.

EXPERIMENTAL

Compounds **4** and **5** were synthesized by the familiar procedures in [9] and [10]. The crystals for the X-ray diffraction studies were obtained by recrystallization of the samples from ethanol; mp 100-101°C for compound **4**, 72-73°C for compound **5**.

The X-ray diffraction experiment was conducted on a Syntex P21 diffractometer, CuKα radiation, with a graphite monochromator. The crystallographic parameters of the crystals are given in Table 1. The structure was deciphered by the direct method using the program SHELXS-86; refinement was by the full-matrix least-squares method using the program SHELXL-93 in the anisotropic approximation, using all $F2$. The coordinates of the hydrogen atoms were refined isotropically and taken from a difference synthesis. The coordinates of the nonhydrogen atoms are given in Tables 2 and 3.

The RHF/6-31 G* calculations were performed using the program GAMESS [11].

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