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CRYSTAL STRUCTURE OF 4,6-DIMETHYL-2-NITRO- AND 2-NITRO-5-PHENYLPYRIMIDINES

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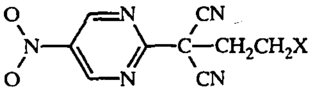
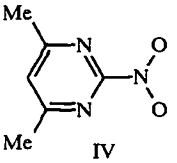
The crystal structures of two substituted 2-nitropyrimidines are solved by X-ray diffraction analysis. The influence of the nitro group and the endocyclic nitrogen atoms on the geometric parameters of the 2-nitropyrimidine and related α-nitroazines are discussed.

Previously we have published X-ray diffraction data for the crystal structure of 2-nitropyridine (I) and compared the obtained geometric parameters with those of nitrobenzene (II) [1]. In continuation of the study of the features of geometry of α-nitroazines, we focused our attention on substituted 2-nitropyrimidines. According to the Cambridge structural database [2] and the literature [3], only substituted 5-nitro derivatives of the nitropyrimidines have been studied. Only two of these, 2-(1,1-dicyanopent-4-yn-1-yl)-5-nitropyrimidine (IIIa) and 5-nitro-2-(1,1,3-tricyanoprop-1-yl)pyrimidine (IIIb) [4], do not have substituents in the 4- and 6-positions neighbouring to the nitro group of the heterocycle.

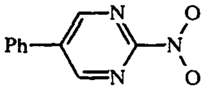
Nitro group in the 5-position of the pyrimidine ring is comparable in chemical and physical characteristics with nitro group in aromatic compounds [5, 6]. 2- And 4-nitropyrimidines are also interesting because the nitrogen atoms of the heterocycle and nitro group affect each other. In particular, this makes the latter highly nucleophilic in the mentioned nitro compounds [7]. Therefore, structural changes in the pyrimidine molecule caused by introduction of nitro group in the α-position to the ring nitrogen atom and in the molecule of nitroaromatic compound are interesting.



IIIa,b



IV



V

a X = C≡CH; b X = CN

In the present work, the crystal structures of 4,6-dimethyl-2-nitropyrimidine (IV) and 2-nitro-5-phenylpyrimidine (V) are solved (Fig. 1).

The crystallographic data for IV and V are given in Table 1. The coordinates of non-hydrogen atoms appear in Tables 2 and 3. The individual bond lengths and angles are listed in Tables 4 and 5. According to the X-ray structure analysis, the nitro group in both compounds deviates from the plane of the pyrimidine ring by 10.7(2) and 10.4(1)°, respectively. The turn of the phenyl group in V is 39.71(5)°. This agrees with the values for 4-nitrodiphenyl (33.0°) [8] and 5-phenylpyrimidine (36.2°) [9].

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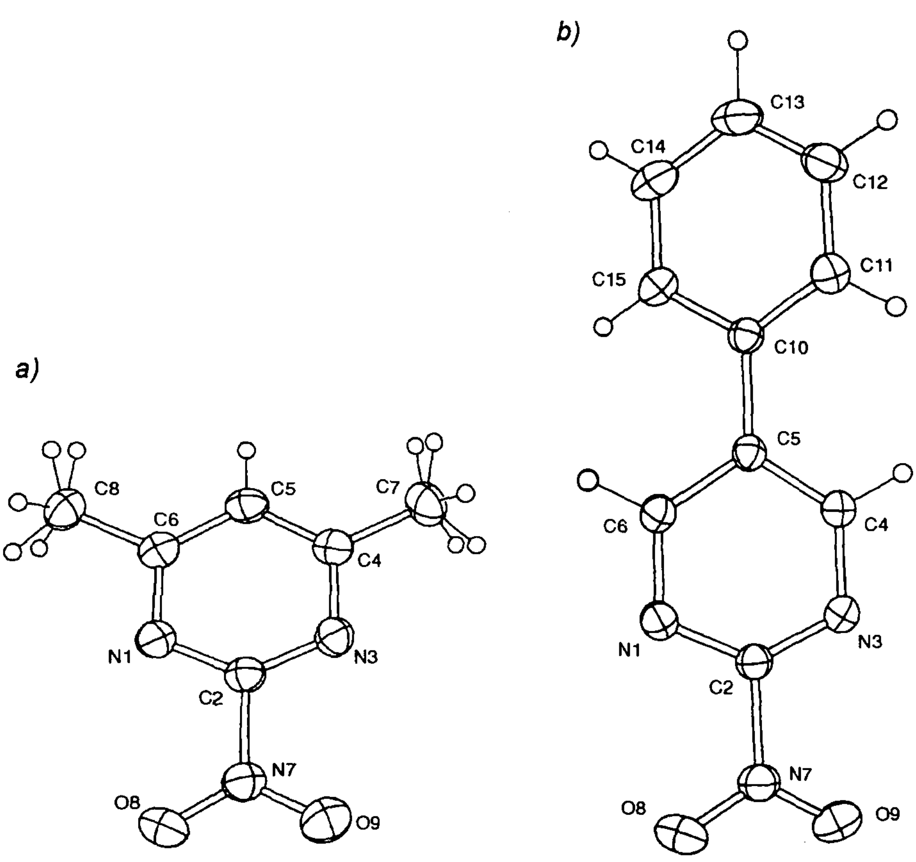

Fig. 1. X-ray structures of 4,6-dimethyl-2-nitropyrimidine IV and 2-nitro-5-phenylpyrimidine V (25% thermal ellipsoids are shown).

The differences in the lengths of formally equivalent bonds in IV and V are less than 3σ. We compared the average bond lengths in the fragments $N_{(1)}$–$C_{(2)}$–$N_{(3)}$, $C_{(2)}$–NO_2, and $O_{(8)}$–$N_{(7)}$–$O_{(9)}$ of IV and V (Table 6) with the statistical average values for the corresponding bonds in aromatic compounds [10] and the average bond lengths for 2-nitropyridine derivatives [1] and compounds IIIa,b [4] in order to reveal the effect of the nitro group and the ring nitrogen atoms on the geometric parameters of the $N_{(1)}$–$C_{(2)}$–NO_2 moiety.

The comparison indicates that introduction of nitro group in the α-position to the ring nitrogen atom results in a concomitant shortening of the ring C–N bond for 2-nitropyrimidines and 2-nitropyridines by 0.021-0.029 Å whereas there are no changes for 5-nitropyrimidines IIIa,b. The C–NO_2 bond length in IIIa,b is the same as the statistical average value for C_{Ar}–NO_2. However, it increases both in 2-nitropyrimidines and in 2-nitropyridines by 0.034 and 0.029 Å, respectively. The N–O bonds in nitropyrimidines and nitropyridines vary little from the statistical average. In 2-nitropyrimidines they are insignificantly shortened (by 0.005 Å); in 5-nitropyrimidines, lengthened by the same amount; and almost unchanged in 2-nitropyridines. Almost the same deviations can be produced by comparing *ab initio* calculations (3-21G basis set) [11] for the bond lengths in pyrimidine, 2-nitropyrimidine and nitrobenzene (bond lengths change by -0.023 Å for N–C–N, by +0.021 for C–NO_2, and by -0.004 Å for N–O). We have performed *ab initio* calculations (6-31G* basis set) for the bond lengths and angles in 4,6-dimethylpyrimidine (VI) and its 2-nitro analog IV and have found that the $N_{(1)}$–$C_{(2)}$ bond length in IV is shorter by 0.019 Å than in 4,6-dimethyl-substituted VI.

The bond angle α at the *ipso*-carbon atom is an important characteristic of the substituent effect on the aromatic (heteroaromatic) ring. The bond angles $N_{(1)}$–$C_{(2)}$–$N_{(3)}$ in pypimidines IV and V are increased in comparison with the unsubstituted pyrimidine. The change in the angle ($\Delta\alpha$) for IV is +4.4°; for V, +3.0° (Table 7). The value of $\Delta\alpha$ for 4-nitropyrimidine V is comparable with the value for nitrobenzene; for IV, it is greater. This may be due to the presence of the methyl substituents in IV. Thus, if the average intracyclic angle α at $C_{(2)}$ for

TABLE 1. Crystal Data for IV and V

Parameter	Compound	
	IV	V
Empirical formula	$C_6H_7N_3O_2$	$C_{10}H_7N_3O_2$
Molecular mass	153,15	201,19
Cell type	Monoclinic	Triclinic
Space group	$P2_{1/c}$	$P\bar{1}$
Cell constants (Å)		
a	3,923(1)	3.8359(7)
b	24.124(6)	10,172(2)
c	7.838(1)	11,778(2)
α	90	96.42(2)
β	101.58(2)	93,93(2)
γ	90	96.77(2)
Cell volume (Å^3)	726.7(3)	451,9(1)
Z	4	2
Crystal dimensions (mm^3)	1.00 × 0,30 × 0,15	0.75 × 0,27 × 0,05
Scanning method	ω	θ/2θ
Region of θ (°)	3...57	3...70
Number of reflections	2605	2105
Number of independent reflections	1081	1725
Absorption correction	Along the face	Along the face
Transmission	0,877...0,671	0.959...0.688
R_1 ($I > 2\sigma$)	0.0435	0,0390
wR_2 (all I)	0.1239	0.1137
S	1,037	1,041
Extinction	0,010(2)	0,066(5)

the series of 2-R-4,6-dimethylpyrimidines {R = $N(CH_3)_2$, $NHCH_3$, SCH_2COOH, S_2-[4,6-$(CH_3)_2$-pyrimidin-2-yl], $NHSO_2C_6H_4NH_2$-*p*} taken from the Cambridge structure database [2] is 128.8(6)°, then Δα for the dimethylderivative IV calculated relative to this average value, is 3.2°. This value is comparable with the change in the angle for nitrobenzene. An analogous result (see Table 7) was obtained using *ab initio* calculations and in the literature [11].

The data reviewed suggest that the nature of the influence of the nitro group and the azine ring in 2-nitropyridines and 2-nitropyrimidines is comparable.

TABLE 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Factors (Å^2×10^3) for Non-hydrogen Atoms of 4,6-Dimethyl-2-nitropyrimidine (IV)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
$N_{(1)}$	7216(4)	5802(1)	346(2)	48(1)
$C_{(2)}$	6550(5)	6241(1)	1213(2)	45(1)
$N_{(3)}$	4832(4)	6697(1)	718(2)	49(1)
$C_{(4)}$	3519(5)	6723(1)	-1014(3)	48(1)
$C_{(5)}$	4012(6)	6288(1)	-2070(3)	51(1)
$C_{(6)}$	5858(5)	5825(1)	-1376(3)	48(1)
$N_{(7)}$	8041(5)	6211(1)	3136(2)	58(1)
$O_{(8)}$	7156(6)	6557(1)	4072(2)	88(1)
$O_{(9)}$	10070(6)	5844(1)	3652(2)	99(1)
$C_{(10)}$	1631(7)	7240(1)	-1678(3)	64(1)
$C_{(11)}$	6449(7)	5335(1)	-2439(3)	64(1)

TABLE 3. Atomic Coordinates ($\times10^4$) and Equivalent Thermal Factors ($\text{Å}^2\times10^3$) of Non-hydrogen Atoms in 2-Nitro-5-phenylpyrimidine (V)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
$N_{(1)}$	3559(3)	1500(1)	9644(1)	41(1)
$C_{(2)}$	3098(4)	2647(1)	9283(1)	38(1)
$N_{(3)}$	1930(4)	3701(1)	9798(1)	42(1)
$C_{(4)}$	1209(4)	3597(1)	10888(1)	40(1)
$C_{(5)}$	1628(4)	2460(1)	11411(1)	35(1)
$C_{(6)}$	2782(4)	1417(1)	10727(1)	39(1)
$N_{(7)}$	4073(4)	2784(1)	8087(1)	50(1)
$O_{(8)}$	5640(4)	1923(1)	7628(1)	74(1)
$O_{(9)}$	3281(5)	3748(1)	7652(1)	76(1)
$C_{(10)}$	839(4)	2348(1)	12611(1)	36(1)
$C_{(11)}$	1731(4)	3431(2)	13460(1)	45(1)
$C_{(12)}$	1014(5)	3296(2)	14582(1)	56(1)
$C_{(13)}$	-658(5)	2113(2)	14858(2)	58(1)
$C_{(14)}$	-1568(5)	1042(2)	14021(2)	53(1)
$C_{(15)}$	-787(4)	1153(2)	12906(1)	43(1)

TABLE 4. Bond Lengths (Å) in Molecules of IV and V

Bond	Compound	
	IV	V
$N_{(1)}$—$C_{(2)}$	1,312(2)	1,313(2)
$C_{(2)}$—$N_{(3)}$	1.308(2)	1,313(2)
$N_{(3)}$—$C_{(4)}$	1,354(3)	1,344(2)
$C_{(4)}$—$C_{(5)}$	1,374(3)	1.390(2)
$C_{(5)}$—$C_{(6)}$	1,382(3)	1,392(2)
$N_{(1)}$—$C_{(6)}$	1,349(3)	1,339(2)
$C_{(2)}$—$N_{(7)}$	1,505(3)	1.499(2)
$N_{(7)}$—$O_{(8)}$	1,208(2)	1,218(2)
$N_{(7)}$—$O_{(9)}$	1,205(2)	1,215(2)

TABLE 5. Bond Angles (deg) in Molecules of IV and V

Angle	Compound	
	IV	V
$N_{(1)}$—$C_{(2)}$—$N_{(3)}$	132,0(2)	130,6(1)
$C_{(2)}$—$N_{(3)}$—$C_{(4)}$	113,9(2)	114,2(1)
$N_{(3)}$—$C_{(4)}$—$C_{(5)}$	119,9(2)	122,5(1)
$C_{(4)}$—$C_{(5)}$—$C_{(6)}$	120,4(2)	115,8(1)
$C_{(5)}$—$C_{(6)}$—$N_{(1)}$	119,8(2)	122,9(1)
$C_{(6)}$—$N_{(1)}$—$C_{(2)}$	114,0(2)	114.0(1)
$N_{(1)}$—$C_{(2)}$—$N_{(7)}$	113,7(2)	115.0(1)
$C_{(2)}$—$N_{(7)}$—$O_{(8)}$	118,3(2)	117,2(1)
$O_{(8)}$—$N_{(7)}$—$O_{(9)}$	123,7(2)	124,9(1)

TABLE 6. Bond Lengths (Å) in Molecules of Nitro Derivatives of Pyridine (Py) and Pyrimidine (Pym)

Bond	Statistical average bond lengths [10]	Average bond lengths			Deviation of average values from statistical average		
		III [4]	IV and V	2-nitropyridines*	III	IV and V	2-nitropyridines*
$N_{(1)}—C_{(2)}—N_{(3)Pym}$	1,333(13)	1.329(7)	1,312(2)	—	-0,004	-0,021	—
$N_{(1)}—C_{(2)Py}$	1.337(12)	—	—	1,308(2)	—	—	-0,029
$C_{(2)}—C_{(3)Py}$	1.379(12)	—	—	1,373(15)	—	—	-0,006
$C—C_{Ar}$	1,384(13)	1,378(9)	1,384(7)	—	-0,006	0,0	—
$C—NO_2$	1,468(14)	1,468(1)	1,502(3)	1,497(5)	0,0	+0,034	+0,029
N—O	1,217(11)	1,222(7)	1,212(5)	1,215(7)	+0,005	-0,005	-+0.002

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* Average values for I [1] and *exo*-6-acetoxy-3-nitro-5,6,7,8-tetrahydro-5,8-methanoquinoline [12].

TABLE 7. Change of Endocyclic Angle at *ipso*-Carbon Atom on Introduction of Nitro Group in the Ring

Compound with nitro group	Parent compound	Angle increase, Δα, deg.	
		X-ray diffraction analysis	calculations
I	Pyridine	3,6 [1]	2,0*
II	Benzene	2,9 [1]	2,0*
IV	Pyrimidine	4,4*	4,7*
IV	4,6-Dimethylpyrimidine (VI)	—	2,3
V	Pyrimidine	3,0*	—
V	5-Phenylpyrimidine	3,1*2	

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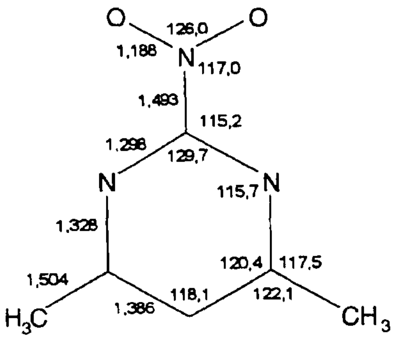
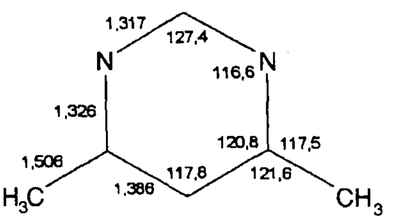
* Calculated for I, II and IV using quantum-chemical calculations [11]; for IV and V, from X-ray diffraction data [13].

*2 The angle $N_{(1)}$–$C_{(2)}$–$N_{(3)}$ for 5-phenylpyrimidine is 127.5(3)° from our data (X-ray diffraction analysis).



IV



VI

EXPERIMENTAL

Compounds IV and V were prepared by oxidation of the corresponding 2-hydroxyaminopyrimidines with ozone by the literature method [14]. Crystals for the structure analysis were grown by recrystallization from ethanol (IV, mp 118-120 °C; V, mp 205-207 °C).

X-ray Structure Analyses of IV and V were carried out on a Syntex $P2_1$ diffractometer using Cu Kα-radiation and a graphite monochromator. The structures were solved by direct method using the SHELXS-86 program and were refined by anisotropic full-matrix least-squares method over all F^2. The hydrogen coordinates were refined isotropically. The hydrogen atoms for the CH_3 groups in IV were calculated geometrically owing to disorder (~1:1). For V, the hydrogen atom coordinates were found in a difference synthesis. Quantum-chemical *ab initio* calculations using the 6-31G* basis set were performed using the GAMESS program [15].

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