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2-Amino-6-methoxy-4,5-di(methoxycarbonyl)pyridine and 2-Amino-4,5-di(methoxycarbonyl)-6-methylthiopyridine

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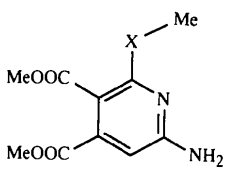
Abstract

The title compounds, dimethyl 5-amino-1-methoxy-2,3-pyridinedicarboxylate, $C_{10}H_{12}N_2O_5$, and dimethyl 5-amino-1-methylthio-2,3-pyridinedicarboxylate, $C_{10}H_{12}N_2O_4S$, are not isomorphous but have similar packing and hydrogen-bonding patterns. Both structures contain hydrogen-bonded ribbons, with van der Waals contacts between the ribbons.

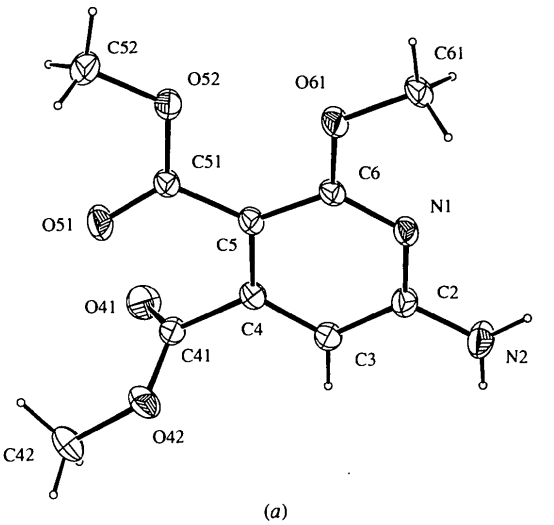
Comment

2-Aminopyridine derivatives constitute a class of nitrogen heterocycles used in the agrochemical and pharmaceutical industries (Vijn, Arts, Maas & Castelijns, 1993). They are also appropriately functionalized to allow preparation of other types of pyridine-fused heterocyclic systems of potential biological interest (Shawcross & Stanforth, 1993; Cobo, Sánchez & Nogueras, 1993). The structures of dimethyl 5-amino-1-methoxy-2,3-pyridinedicarboxylate, (I), and dimethyl 5-amino-1-methylthio-2,3-pyridinedicarboxylate, (II), have been determined.

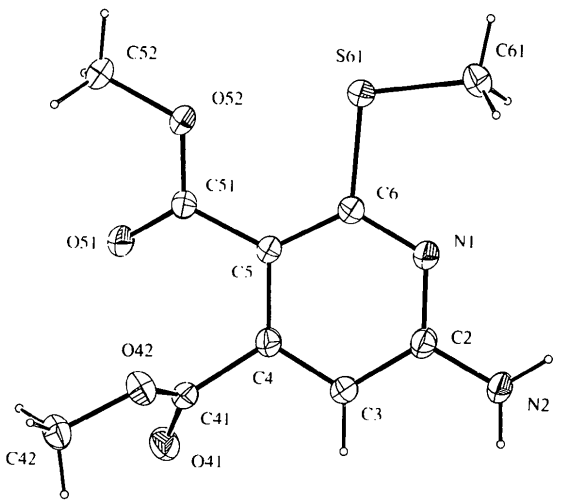


(I) X = O
(II) X = S

Views of compounds (I) and (II) are shown in Figs. 1(*a*) and (*b*), respectively. If the 6-methoxy and 6-methylthio residues are excluded, the molecular dimensions (Tables 2 and 4) show that there is very little difference between the two molecules, *i.e.* in the range 0.001–0.015 Å, mean difference 0.006 Å.



(*a*)



(*b*)

Fig. 1. Views of (*a*) compound (I) and (*b*) compound (II) with their atomic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level.

The molecules, however, differ markedly in conformation, with the methoxycarbonyl residues at atoms C4 and C5 having quite different torsion angles [C4—C5—C51—O51 12.4 (2)° in (I) and −16.1 (2)° in (II), and C5—C4—C41—O41 81.4 (2)° in (I) and 119.7 (2)° in (II)].

In both structures, the molecules are linked by N—H···O hydrogen bonds to form base pairs related by an inversion centre. These pairs are then further linked about other inversion centres to form hydrogen-bonded ribbons; geometrical details are given in Tables 2 and 4. Contacts between the ribbons correspond with van der Waals contacts.

Experimental

Compounds (I) and (II) were synthesized according to Cobo, García, Melguizo, Sánchez & Nogueras (1994).

Compound (I)

Crystal data

$C_{10}H_{12}N_2O_5$
M_r = 240.22
Triclinic
$P\bar{1}$
a = 7.2245 (15) Å
b = 8.7974 (13) Å
c = 9.181 (2) Å
α = 81.627 (13)°
β = 80.521 (13)°
γ = 76.580 (15)°
V = 556.3 (2) Å^3
Z = 2
D_x = 1.434 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.5–17.0°
μ = 0.117 mm^{-1}
T = 294 (1) K
Prism
0.40 × 0.26 × 0.25 mm
Light yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2417 measured reflections
2417 independent reflections
1813 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 26.91°
$h = -8 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.5%

Refinement

Refinement on F^2
$R(F)$ = 0.0468
$wR(F^2)$ = 0.1408
S = 1.127
2417 reflections
154 parameters
H atoms riding (*SHELXL93* defaults, C—H 0.93–0.96, N—H 0.86 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0842P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.038
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (I)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.2417 (2)	0.87926 (15)	0.57814 (15)	0.0345 (3)
C2	0.2160 (3)	0.8419 (2)	0.7263 (2)	0.0359 (4)
N2	0.2076 (3)	0.6919 (2)	0.7764 (2)	0.0523 (5)
C3	0.1993 (3)	0.9531 (2)	0.8257 (2)	0.0362 (4)
C4	0.2086 (2)	1.1040 (2)	0.7680 (2)	0.0319 (4)
C41	0.1755 (3)	1.2217 (2)	0.8792 (2)	0.0354 (4)
O41	0.0215 (2)	1.30370 (15)	0.91396 (14)	0.0500 (4)
O42	0.3310 (2)	1.21062 (15)	0.94178 (14)	0.0478 (4)
C42	0.3159 (4)	1.3164 (3)	1.0522 (2)	0.0607 (6)
C5	0.2346 (2)	1.1482 (2)	0.6141 (2)	0.0305 (4)
C51	0.2523 (2)	1.3109 (2)	0.5614 (2)	0.0319 (4)
O51	0.2769 (2)	1.39726 (14)	0.64476 (14)	0.0541 (4)
O52	0.2382 (2)	1.35690 (14)	0.41979 (14)	0.0503 (4)
C52	0.2615 (3)	1.5158 (2)	0.3677 (2)	0.0524 (5)
C6	0.2509 (2)	1.0260 (2)	0.5250 (2)	0.0305 (4)
O61	0.2786 (2)	1.06012 (13)	0.37723 (12)	0.0397 (3)
C61	0.2848 (3)	0.9359 (2)	0.2888 (2)	0.0411 (4)

Table 2. *Selected geometric parameters (Å, °) for* (I)

N1—C2	1.345 (2)	O42—C42	1.448 (2)
N1—C6	1.325 (2)	C5—C6	1.416 (2)
N2—C2	1.344 (2)	C5—C51	1.471 (2)
C2—C3	1.405 (2)	O51—C51	1.213 (2)
C3—C4	1.368 (2)	O52—C51	1.317 (2)
C4—C5	1.403 (2)	O52—C52	1.449 (2)
C4—C41	1.511 (2)	O61—C6	1.338 (2)
O41—C41	1.199 (2)	O61—C61	1.442 (2)
O42—C41	1.322 (2)		
C6—C5—C51	126.61 (14)	N1—C6—C5	124.34 (14)
C3—C4—C41—O41	−94.4 (2)	C6—C5—C51—O51	−164.0 (2)
C5—C4—C41—O41	81.4 (2)	C4—C5—C51—O52	−167.0 (2)
C3—C4—C41—O42	79.4 (2)	C6—C5—C51—O52	16.5 (2)
C5—C4—C41—O42	−104.7 (2)	N1—C6—O61—C61	3.5 (2)
C4—C5—C51—O51	12.4 (2)	C5—C6—O61—C61	−176.87 (14)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O51^{i}	0.86	2.12	2.922 (2)	156
N2—H2B···O41^{ii}	0.86	2.31	3.045 (2)	144

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, 2-y, 2-z$.

Compound (II)

Crystal data

$C_{10}H_{12}N_2O_4S$
M_r = 256.28
Triclinic
$P\bar{1}$
a = 8.0720 (10) Å
b = 8.6448 (14) Å
c = 8.990 (2) Å
α = 94.35 (2)°
β = 111.133 (13)°
γ = 91.703 (13)°
V = 582.4 (2) Å^3
Z = 2
D_x = 1.461 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10.0–18.0°
μ = 0.283 mm^{-1}
T = 294 (1) K
Prism
0.38 × 0.35 × 0.29 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2530 measured reflections
2530 independent reflections
2126 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 26.89°
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity decay: no decay, variation 0.6%

Refinement

Refinement on F^2
$R(F)$ = 0.0347
$wR(F^2)$ = 0.0959
S = 1.033
2530 reflections
154 parameters
H atoms riding (*SHELXL93* defaults, C—H 0.93–0.96, N—H 0.86 Å)

$w = 1/[\sigma^2(F_o^2) + (0.0556P)^2 + 0.1212P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for* (II)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
N1	0.7275 (2)	0.47172 (15)	0.99964 (14)	0.0346 (3)
C2	0.6639 (2)	0.3258 (2)	0.9417 (2)	0.0359 (3)
N2	0.6334 (2)	0.2839 (2)	0.7863 (2)	0.0505 (4)
C3	0.6323 (2)	0.2167 (2)	1.0382 (2)	0.0375 (3)
C4	0.6584 (2)	0.2645 (2)	1.1937 (2)	0.0319 (3)
C41	0.6328 (2)	0.1418 (2)	1.2946 (2)	0.0334 (3)
O41	0.4930 (2)	0.07147 (14)	1.27038 (13)	0.0458 (3)
O42	0.78704 (15)	0.11255 (13)	1.40408 (13)	0.0415 (3)
C42	0.7789 (3)	0.0030 (2)	1.5151 (2)	0.0473 (4)
C5	0.7168 (2)	0.4191 (2)	1.2568 (2)	0.0305 (3)
C51	0.7241 (2)	0.4630 (2)	1.4214 (2)	0.0314 (3)
O51	0.6490 (2)	0.38546 (13)	1.48672 (13)	0.0433 (3)
O52	0.8200 (2)	0.59449 (13)	1.49093 (12)	0.0425 (3)
C52	0.8275 (2)	0.6399 (2)	1.6519 (2)	0.0432 (4)
C6	0.7545 (2)	0.5173 (2)	1.1528 (2)	0.0316 (3)
S61	0.84473 (6)	0.70968 (5)	1.21952 (5)	0.04283 (14)
C61	0.8692 (3)	0.7755 (2)	1.0434 (2)	0.0511 (4)

Table 4. *Selected geometric parameters (Å, °) for* (II)

N1—C2	1.340 (2)	O42—C42	1.443 (2)
N1—C6	1.340 (2)	C5—C6	1.413 (2)
N2—C2	1.347 (2)	C5—C51	1.479 (2)
C2—C3	1.406 (2)	O51—C51	1.206 (2)
C3—C4	1.365 (2)	O52—C51	1.332 (2)
C4—C5	1.409 (2)	O52—C52	1.450 (2)
C4—C41	1.502 (2)	S61—C6	1.766 (2)
O41—C41	1.205 (2)	S61—C61	1.796 (2)
O42—C41	1.325 (2)		
C6—C5—C51	127.07 (13)	N1—C6—C5	123.11 (13)
C3—C4—C41—O41	−64.2 (2)	C5—C4—C41—O42	−65.8 (2)
C5—C4—C41—O41	119.7 (2)	N1—C6—S61—C61	−0.40 (14)
C3—C4—C41—O42	110.4 (2)	C5—C6—S61—C61	178.67 (13)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O51^{i}	0.86	2.20	2.939 (2)	145
N2—H2B···O41^{ii}	0.86	2.33	3.153 (2)	160

Symmetry codes: (i) $x, y, z-1$; (ii) $1-x, -y, 2-z$.

For both compounds, only a unique data set was collected. The diagrams [Figs. 1(*a*) and (*b*)] were prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*) and the packing plots [Figs. 2(*a*) and (*b*), in deposit material] were prepared with *PLUTON* (Spek, 1995*b*). Examination of the structure with *PLATON* showed that there were no solvent-accessible voids in the crystal lattice.

For both compounds, data collection: *CAD-4/PC Software* (Enraf–Nonius, 1992); cell refinement: Enraf–Nonius *SET*4 (de Boer & Duisenberg, 1984) and *CELDIM*; data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985) for (I); *SOLVER* in *NRCVAX* for (II). For both compounds, program(s) used to refine structures: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94, *PLATON* and *PLUTON*; software used to prepare material for publication: *NRCVAX*94, *SHELXL*93 and WordPerfect.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles, together with packing diagrams for both compounds, have been deposited with the IUCr (Reference: AB1308). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-Methoxy-4,5-di(methoxycarbonyl)-2-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-aminopyridine and 4,5-Di(methoxycarbonyl)-6-methylthio-2-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)aminopyridine

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(*Received 16 August 1995; accepted 11 September 1995*)

Abstract

The title compounds, dimethyl 2-methoxy-6-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)amino-3,4-pyridinedi-