Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N—S1 | 1.6552 (15) | N—S2 | 1.6578 (15) |
| S1—N—S2 | 124.97 (10) | H01—N—S2 | 111 (1) |
| H01—N—S1 | 115 (1) | | |

| | |
|---|---|
| S2—N—S1—O1 | 176.56 (10) |
| S2—N—S1—O2 | 48.44 (12) |
| S2—N—S1—C11 | −68.21 (12) |
| S1—N—S2—O3 | 160.72 (10) |
| S1—N—S2—O4 | 31.44 (13) |
| S1—N—S2—C21 | −85.81 (11) |
| N—S1—C11—C12 | −55.43 (15) |
| N—S2—C21—C22 | −46.71 (16) |
| O31—C32—C33—O34 | 73.49 (19) |
| C32—C33—O34—C35 | −153.49 (15) |
| C33—O34—C35—C36 | 97.73 (18) |
| O34—C35—C36—O31$^{i}$ | −76.43 (19) |
| C35—C36—O31$^{i}$—C32$^{i}$ | 161.40 (15) |
| C36—O31$^{i}$—C32$^{i}$—C33$^{i}$ | −94.79 (18) |

Symmetry code: (i) $2-x, 1-y, 1-z$.

H atoms were initially placed in geometrically calculated positions, except for the amino H atom, which was found in a difference Fourier synthesis. During refinement, these H atoms were refined freely and constrained to ride on their parent C atoms, respectively. For all H atoms, $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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# 2-Dicyanomethylene-5,6-dimethyl-1,2-dihydropyridine-3-carbonitrile†

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## Abstract

The title compound, $C_{11}H_8N_4$, exists as the NH tautomer (a 1,2-dihydropyridine) in the solid state, although the bond-length differences in the ring are minimal (thus implying delocalized multiple bonding). Molecules are linked in pairs by N—H···N hydrogen bonds over inversion centres.

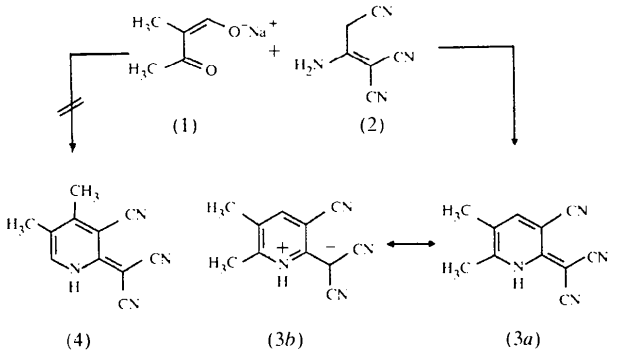
## Comment

We have described several novel syntheses of 2(1*H*)-pyridinethiones (Elgemeie *et al.*, 1990; Elgemeie, Elzanate & Mansour, 1992; Elgemeie, Alnaimi & Alarab, 1992). These compounds, as well as a number of suitably functionalized pyridine derivatives, are considered important intermediates for the synthesis of various

† Zwitterionic name: (3-cyano-5,6-dimethyl-2-pyridinio)dicyanomethanide.

5-deaza analogues of the pteridine and folic acid ring systems (Elgemeie & Hussain, 1994). The latter have a greater selectivity for a broader range of human tumors and are used clinically (Taylor *et al.*, 1989; Gangjee *et al.*, 1996).

As a continuation of this work, the title compound, (3), was prepared as a precursor for the synthesis of other antimetabolites. The sodium salt of 3-(hydroxymethylene)-2-butanone, (1), reacted with 2-amino-1,1,3-tricyanopropene, (2), to give a tetrasubstituted pyridine. Two modes of cyclization are feasible, giving a 2,3,4,5- or 2,3,5,6-tetrasubstituted product, as outlined in the scheme. In fact, only one isomer was obtained; the spectra did not allow us to distinguish between structures (3) and (4). $^1$H NMR revealed the presence of a broad NH signal at $\delta$ = 11.67 p.p.m. in solution. No significant amounts of the alternative tautomer could be detected. In order to establish unambiguously the structure of the product, the crystal structure was determined.




The X-ray analysis (Fig. 1) confirms the exclusive presence of the aromatic pyridinium tautomer (3*b*) in the solid state; all H atoms could be located unambiguously. The ring bond lengths are not consistent with localized double and single bonds. This suggests a modification of the non-aromatic formula (3*a*) such that the N1 atom acquires a formal positive charge, the ring electrons are delocalized and the negative charge is delocalized over the CN groups. The preferential formation of (3*b*) can be interpreted in terms of (i) the high degree of resonance stability of systems related to $\alpha$-pyridone and (ii) the presence of three electron-withdrawing cyano groups adjacent to the ring N atom, which would tend to delocalize its lone pair. The C1—C6 bond length of 1.405 (4) Å lends support to this view, lying between expected values for double and single bonds.

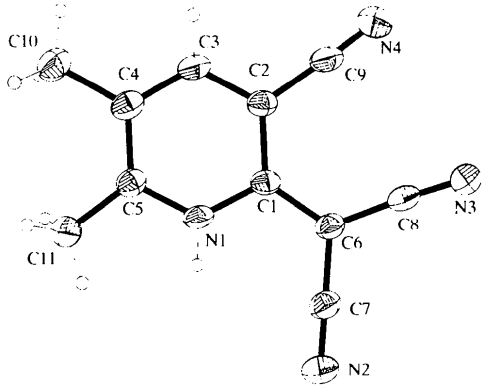



Fig. 1. The molecule of the title compound in the crystal. Ellipsoids represent 50% probability and H-atom radii are arbitrary.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed very few comparable systems. Polymorphs of the antibacterial drug sulfapyridine (Bernstein, 1988, and references therein), in which the pyridine ring bears a 2-$NSO_2R$ substituent, were assigned a structure analogous to tautomer (3*b*), as was bis(6-methoxymethyl-2-pyridyl)acetonitrile (Newkome *et al.*, 1988); although the H atoms at nitrogen were located, the differences in length between formal single and double bonds were not great. A related ring system bearing a 3-$SO_2NR$ group was established as a zwitterion, with a pyridinium ring and an exocyclic $N^-$ (Dupont *et al.*, 1995).

The six-membered ring of the title compound is planar [r.m.s. deviation 0.014 Å]; the substituent atoms C9 and C11 show appreciable displacement from the plane [0.131 (4) and 0.105 (5) Å, respectively]. The dicyanomethylene group is rotated slightly with respect to the ring plane, as shown by the torsion angle C2—C1—C6—C8 of 8.2 (4)°.

The molecules are connected in pairs about an inversion centre by N—H···N hydrogen bonds, with N1—H1 0.87 (3), N1···N2$^i$ 3.087 (4), H1···N2$^i$ 2.30 (3) Å and N1—H1···N2$^i$ 150 (3)° [symmetry code: (i) $2-x$, $1-y$, $1-z$].

## Experimental

A solution of 3-(hydroxymethylene)-2-butanone [0.01 mol; (1)], 2-amino-1,1,3-tricyanopropene [0.01 mol; (2)] and piperidine acetate (1 ml) in water (5 ml) and ethanol (30 ml) was refluxed for 15 min. Acetic acid (1.5 ml) was added to the resulting hot solution. The precipitated solid was collected by filtration and crystallized from ethanol in 80% yield; m.p. > 573 K.

*Crystal data*

$C_{11}H_8N_4$
$M_r$ = 196.21
Monoclinic
$P2_1/n$
$a$ = 7.712 (3) Å
$b$ = 11.579 (4) Å
$c$ = 11.416 (4) Å
$\beta$ = 106.11 (3)°
$V$ = 979.4 (6) Å$^3$
$Z$ = 4
$D_x$ = 1.331 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 48 reflections
$\theta$ = 10.0–11.5°
$\mu$ = 0.086 mm$^{-1}$
$T$ = 143 (2) K
Needle
0.70 × 0.25 × 0.15 mm
Yellow

*Data collection*

| | |
|---|---|
| Stoe Stadi-4 diffractometer | $\theta_{max} = 25.02°$ |
| $\omega/\theta$ scans | $h = -9 \rightarrow 0$ |
| Absorption correction: none | $k = -13 \rightarrow 3$ |
| 2432 measured reflections | $l = -13 \rightarrow 13$ |
| 1726 independent reflections | 3 standard reflections |
| 1163 reflections with $I > 2\sigma(I)$ | frequency: 60 min |
| | intensity decay: none |
| $R_{int} = 0.024$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.5865P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.054$ | |
| $wR(F^2) = 0.143$ | |
| $S = 1.018$ | $(\Delta/\sigma)_{max} = 0.006$ |
| 1726 reflections | $\Delta\rho_{max} = 0.232$ e Å$^{-3}$ |
| 142 parameters | $\Delta\rho_{min} = -0.199$ e Å$^{-3}$ |
| H atoms treated by a mixture of independent and constrained refinement | Extinction correction: none |
| | Scattering factors from *International Tables for Crystallography* (Vol. C) |

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—C5 | 1.364 (3) | C2—C3 | 1.387 (4) |
| N1—C1 | 1.367 (3) | C3—C4 | 1.385 (4) |
| C1—C6 | 1.405 (4) | C4—C5 | 1.385 (4) |
| C1—C2 | 1.418 (3) | | |
| C5—N1—C1 | 126.3 (2) | C4—C3—C2 | 123.1 (2) |
| N1—C1—C2 | 114.5 (2) | C5—C4—C3 | 116.9 (2) |
| C3—C2—C1 | 119.9 (2) | N1—C5—C4 | 119.1 (3) |

For the H-atom treatment, H1 was refined freely, the methyl H atoms were kept rigid and H3 was refined as riding.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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# 2-Methyl-2-(10-phenoxazinyl)propiononitrile

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## Abstract

The title compound, $C_{16}H_{14}N_2O$, adopts a folded conformation, with a dihedral angle of 145.0 (1)° between the phenyl-ring mean planes, similar to other molecules belonging to the same family.

## Comment

Phenoxazine derivatives have been studied particularly for their therapeutic activities (Ionescu & Mantsch, 1967; Mylari *et al.*, 1990; Palmer *et al.*, 1988). Besides their potential pharmacological applications, phenoxazine derivatives have also been used for their antioxidant and stabilizant actions (Fukuzumi *et al.*,