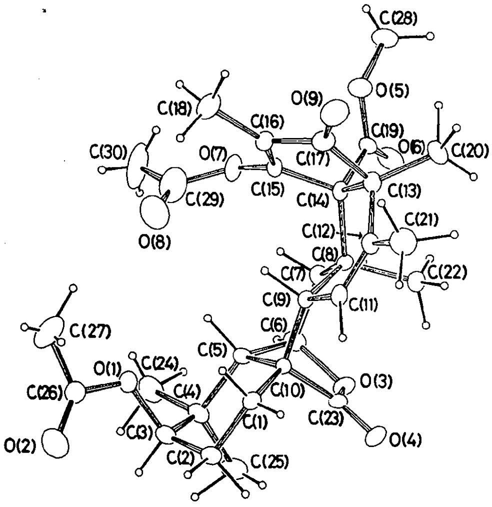

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the molecule with 20% probability ellipsoids. H atoms are represented by circles of radius 0.08 Å.

**Related literature.** Citreohybridone A and B are new sesterterpenoid-type metabolites of a hybrid strain KO 0031 derived from *Penicillium citreo-viride* B. (IFO 6200 and 4692) (Kosemura, Matsunaga, Yamamura, Kubota & Ohba, 1991).

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# Structure of 2-(4-Aminophenyl)-1,3-propanedinitrile

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**Abstract.** $C_9H_7N_3$, $M_r = 157.17$, orthorhombic, $Pna2_1$, $a = 8.758$ (5), $b = 16.795$ (6), $c = 5.646$ (4) Å, $V = 831$ (1) Å$^3$, $Z = 4$, $D_x = 1.257$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.75$ cm$^{-1}$, $F(000) = 328$, $T = 296$ K, $R = 0.044$, 475 unique observed reflections. The solid-state structure for 2-(4-aminophenyl)-1,3-propanedinitrile indicates that an H atom is bound at C(2).

**Experimental.** The title compound was prepared following the procedure of Hartzler (1964). A solution of acetone (20 cm$^3$), Raney nickel active catalyst (1.8 g) and 4-nitrophenylmalononitrile (2.5 g, 0.013 mol) was subjected to $3.45 \times 10^5$ Pa of hydrogen for $2\frac{1}{2}$ h in a Parr apparatus, at room temperature with agitation. The solution was then concentrated to give deep orange needles which were washed with water and recrystallized from a boiling ethanol:water (1:1) mixture. The isolated needles (1.14 g, 56% yield) melted at 408–409 K (lit. 408–409 K; Hartzler, 1964). NMR ($CDCl_3$): $\delta$ 7.237, 7.204, 6.721, 6.693 (*AA'BB'*, 4H), $\delta$ 4.905 (*s*, 1H), $\delta$ 3.89 (broad *s*).

The crystal used for data collection was an orange fragment with dimensions $0.27 \times 0.22 \times 0.13$ mm. Data were collected with a Rigaku AFC5S diffractometer using graphite-monochromated Mo $K\alpha$ radiation, $\omega$–$2\theta$ scans, and a scan speed of 4° min$^{-1}$ (in $\omega$). Weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of two rescans) and the counts accumulated to assure improved counting statistics. The lattice parameters were obtained from a least-squares fit of 25 strong reflections in the $2\theta$ range 20–29°. A total of 814 reflections were measured ($h$ 0 to 10, $k$ 0 to 19, $l$ 0 to 6) [$(\sin\theta/\lambda)_{\max} = 0.60$ Å$^{-1}$] and 339 reflections were considered unobserved with [$I <$

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$B_{eq} = (8\pi^2/3)$ trace **U**.

| | $x$ | $y$ | $z$ | $B_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| N(1) | 1.3431 (5) | 0.1447 (3) | 0.6488 | 6.8 (4) |
| N(3) | 1.0871 (8) | 0.2759 (3) | 1.168 (2) | 7.7 (4) |
| N(4) | 0.6107 (6) | −0.0257 (4) | 0.701 (2) | 5.5 (3) |
| C(1) | 1.2308 (6) | 0.1740 (3) | 0.697 (2) | 4.2 (3) |
| C(2) | 1.0815 (6) | 0.2082 (3) | 0.755 (2) | 3.4 (3) |
| C(3) | 1.0879 (8) | 0.2468 (4) | 0.985 (2) | 4.3 (3) |
| C(1′) | 0.9566 (5) | 0.1453 (3) | 0.742 (2) | 2.8 (2) |
| C(2′) | 0.9404 (6) | 0.0878 (3) | 0.915 (2) | 3.8 (3) |
| C(3′) | 0.8280 (6) | 0.0308 (3) | 0.900 (2) | 3.9 (3) |
| C(4′) | 0.7286 (5) | 0.0296 (3) | 0.713 (2) | 3.8 (3) |
| C(5′) | 0.7441 (6) | 0.0872 (3) | 0.534 (2) | 3.9 (3) |
| C(6′) | 0.8584 (5) | 0.1440 (3) | 0.552 (2) | 3.3 (2) |
| H(2) | 1.060 (5) | 0.249 (3) | 0.64 (1) | 4.1* |
| H(2′)† | 1.0083 | 0.0876 | 1.0451 | 4.6* |
| H(3′)† | 0.8192 | −0.0081 | 1.0210 | 4.6* |
| H(5′)† | 0.6769 | 0.0873 | 0.4012 | 4.7* |
| H(6′)† | 0.8691 | 0.1828 | 0.4305 | 4.0* |
| H(4*a*) | 0.625 (6) | −0.072 (3) | 0.79 (1) | 6.6* |
| H(4*b*) | 0.566 (7) | −0.036 (4) | 0.57 (1) | 6.6* |

* Calculated as 1.2 × $B_{eq}$ of associated C or N atom.

† Calculated atomic coordinates.

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and their e.s.d.'s*

| | | | |
|---|---|---|---|
| N(1)—C(1) | 1.133 (6) | C(2)—H(2) | 0.97 (5) |
| N(3)—C(3) | 1.143 (7) | C(1′)—C(2′) | 1.378 (8) |
| N(4)—C(4′) | 1.391 (6) | C(1′)—C(6′) | 1.375 (7) |
| N(4)—H(4*a*) | 0.95 (5) | C(2′)—C(3′) | 1.376 (7) |
| N(4)—H(4*b*) | 0.87 (7) | C(3′)—C(4′) | 1.373 (7) |
| C(1)—C(2) | 1.465 (7) | C(4′)—C(5′) | 1.403 (8) |
| C(2)—C(3) | 1.451 (8) | C(5′)—C(6′) | 1.387 (6) |
| C(2)—C(1′) | 1.522 (6) | | |

| | | | |
|---|---|---|---|
| C(4′)—N(4)—H(4*a*) | 115 (4) | C(2)—C(1′)—C(2′) | 121.8 (5) |
| C(4′)—N(4)—H(4*b*) | 120 (4) | C(2)—C(1′)—C(6′) | 119.8 (5) |
| H(4*a*)—N(4)—H(4*b*) | 113 (5) | C(2′)—C(1′)—C(6′) | 118.3 (4) |
| N(1)—C(1)—C(2) | 177.1 (5) | C(1′)—C(2′)—C(3′) | 121.4 (5) |
| C(1)—C(2)—C(3) | 109.9 (5) | C(2′)—C(3′)—C(4′) | 120.6 (5) |
| C(1)—C(2)—C(1′) | 111.1 (4) | N(4)—C(4′)—C(3′) | 121.2 (6) |
| C(1)—C(2)—H(2) | 107 (3) | N(4)—C(4′)—C(5′) | 119.8 (6) |
| C(3)—C(2)—C(1′) | 112.3 (5) | C(3′)—C(4′)—C(5′) | 118.9 (5) |
| C(3)—C(2)—H(2) | 108 (3) | C(4′)—C(5′)—C(6′) | 119.4 (5) |
| C(1′)—C(2)—H(2) | 109 (3) | C(1′)—C(6′)—C(5′) | 121.4 (5) |
| N(3)—C(3)—C(2) | 177.2 (8) | | |

$2\sigma(I)$], leaving a data set comprised of 475 unique reflections. Three standard reflections ($\bar{2}\bar{3}0$, $\bar{2}30$, $\bar{1}31$) changed by −0.1, −2.9 and 1.5%, respectively; no decay correction was applied. The data were corrected for Lorentz and polarization; no absorption correction was applied. The direct-methods program *MITHRIL* (Gilmore, 1984) provided the locations of all non-H atoms. Full-matrix least-squares refinement was performed to minimize $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/\mathrm{Lp}^2$ ($S$ = scan rate, $C$ = total integrated peak count, $R$ = ratio of scan time to background counting time, $B$ = total background count, Lp = Lorentz–polarization factor and $p$ = 0.03). After convergence the ring-H atoms were placed at idealized positions (C—H = 0.95 Å) and fixed. The locations of the three remaining H atoms were obtained from a difference Fourier synthesis. The final stages of refinement were performed with 118 variables including all non-H positional and anisotropic thermal parameters, the positional parameters of the non-ring H atoms, a secondary-extinction coefficient [0.5 (1) × $10^{-5}$] and one scale factor. All H-atom $B$ values were calculated and fixed at values equal to 1.2 × $B_{eq}$ of their associated C or N atom. Convergence yielded $R = 0.044$, $wR = 0.040$, $S = 1.20$ and $(\Delta/\sigma)_{max} = 0.01$. Refinement of the alternative polarity along $z$ yielded identical results, thus the absolute configuration was not established. The final difference Fourier synthesis produced $(\Delta\rho)_{max} = 0.14$ and $(\Delta\rho)_{min} = -0.19$ e Å$^{-3}$. Atomic scattering factors and anomalous-dispersion

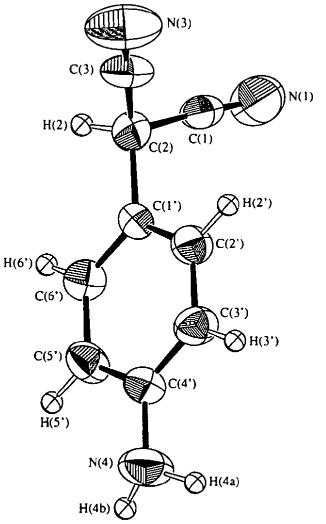

Fig. 1. Molecular configuration and IUPAC atom-numbering scheme, thermal ellipsoids at the 50% probability level. H atoms shown as isotropic spheres with $B$ values of 1.0 Å$^2$.

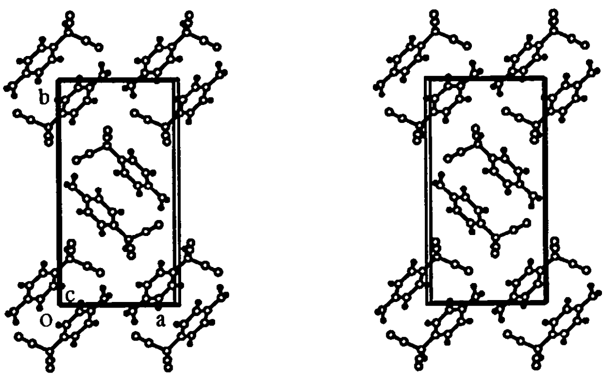

Fig. 2. Stereoscopic illustration of the molecular packing as viewed down the $c$ crystallographic axis.

corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 71, 148). All computer programs were from the *TEXSAN* package (Molecular Structure Corporation, 1985). Table 1 lists the final atomic coordinates and equivalent isotropic temperature factors; Table 2 presents selected interatomic distances and angles.* Fig. 1 shows the atom-numbering scheme and the thermal motion of the molecule; Fig. 2 illustrates the molecular packing.

**Related literature.** Equilibrium acidity data [p$K_a$ values in dimethyl sulfoxide (DMSO) solution] for five variously *G*-substituted aryl-1,3-propanedinitriles (where $G$ = 3-CN, 4-Cl, 4-H, 4-$CH_3$, 4-$OCH_3$) as well as the title compound ($G$ = 4-$NH_2$) are 1.9, 3.14, 4.24, 4.85, 5.68 (Arnett, Chawla, Amarnath & Whitesell, 1987) and 7.24 (Jirka, 1989), respectively. These acidity data plot linearly with Hammett $\sigma$. It is therefore likely that the title compound is deprotonated at C(2), rather than at N(4), in DMSO solution. The X-ray structure for the title compound indicates that an H atom is bound at C(2).

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* Lists of structure factors, anisotropic thermal parameters, intermolecular distances, torsion angles and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54580 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0366]

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# *N*-(4,6-Diméthylpyridin-2-yl)benzènethiocarboxamide

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**Abstract.** $C_{14}H_{14}N_2S$, $M_r = 242.3$, monoclinic, $C2/c$, $a = 20.004\,(2)$, $b = 7.997\,(1)$, $c = 15.954\,(1)$ Å, $\beta = 90.40\,(1)°$, $V = 2552.2\,(7)$ Å$^3$, $Z = 8$, $D_x = 1.261$ Mg m$^{-3}$, $\lambda$(Cu $K\bar{\alpha}$) = 1.5418 Å, $\mu = 2.0$ mm$^{-1}$, $F(000) = 1024$, $T = 295\,(1)$ K, $R = 0.039$ for 1807 independent observed reflections. There is a delocalized orbital over the N—C═S thioamide group. The pyridinyl and the phenyl rings are approximately planar and the dihedral angles between their least-squares planes and the NCS thioamide plane are 25.2 (2) and 44.2 (2)° respectively. The molecules form pairs in which they are linked to each other by two weak N(7)—H(7)···N(1$^{\rm i}$) hydrogen bonds [3.192 (3) Å, 177 (3)°] (i: $-x$, $y$, $\frac{3}{2} - z$). The title compound shows only a very moderate anti-inflammatory activity, even though it is the thio analog of *N*-(4,6-dimethylpyridin-2-yl)benzamide which is a non-acidic compound exhibiting a potent anti-inflammatory activity.

**Partie expérimentale.** Cristal parallélépipédique: 0,13 × 0,22 × 0,26 mm. Dimensions de la maille déterminées avec 25 réflexions pour lesquelles $17{,}55 \leq \theta \leq 32{,}40°$. Diffractomètre Enraf–Nonius CAD-4, balayage $\theta/2\theta$, $0{,}023 \leq (\sin\theta)/\lambda \leq 0{,}573$ Å$^{-1}$; $0 \leq h \leq 22$, $0 \leq k \leq 9$, $-18 \leq l \leq 17$. Réflexions de contrôle de l'intensité: $10,\bar{2},1$, $11\bar{7}$ et $\bar{5}\bar{1}7$. Variations non significatives de $I$ au cours des mesures. 2007 réflex-

0108-2701/92/030556-03$03.00