

2,4,6-Trimethylpyridine-3,5-dicarbonitrile

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Key indicators

Single-crystal X-ray study
 $T = 292\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.059
 wR factor = 0.164
Data-to-parameter ratio = 17.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

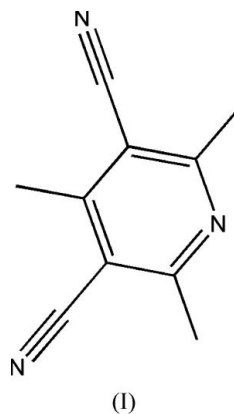
The title compound, $\text{C}_{10}\text{H}_9\text{N}_3$, is essentially planar, except for the methyl H atoms. The asymmetric unit consists of two molecules. In the crystal structure, weak intramolecular $\text{C}-\text{H}\cdots\text{N}$ hydrogen-bonding interactions occur, linking the molecules into chains propagating along the a axis.

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Comment

Organic second-order non-linear optical (NLO) materials have attracted much attention in the past two decades due to their potential applications involving telecommunications, optical data storage and optical information processing (Marder *et al.*, 1997). This interest has led to extensive explorations of 'push-pull' type chromophores with high molecular second-order non-linearity (β) (Alain *et al.*, 1999). Among the three molecular building blocks commonly used for NLO chromophores (electron donor, conjugating bridge and electron acceptor), the development of electron donors and conjugating bridges is already quite mature, such that they can meet most of the synthetic and physical requirements. Therefore, one of the major tasks for optimizing the $\mu\beta$ values (μ is a dipole moment) of a chromophore is the development of novel electron acceptors.



The title compound, (I), is a strong electron acceptor for non-linear optics, and with its excellent electron-withdrawing power, chromophores with (I) as acceptors have been reported to possess exceptionally large third-order non-linear optical effects (Wang *et al.*, 2005). As a part of a project to develop new second-order non-linear optical materials for electron optics applications, we have synthesized (I), following the procedure of Attias *et al.* (2002), and determined its crystal structure.

In the structure of (I) (Fig. 1), the whole molecule is essentially planar, except the methyl H atoms. The asymmetric

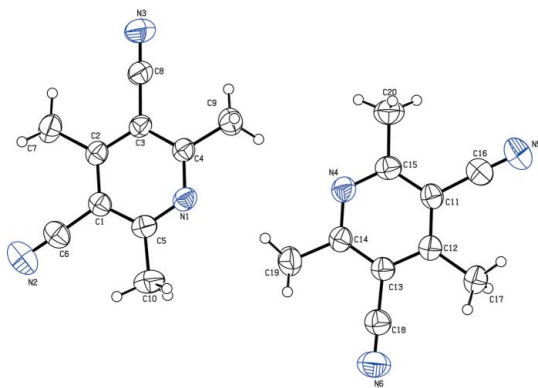


Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level.

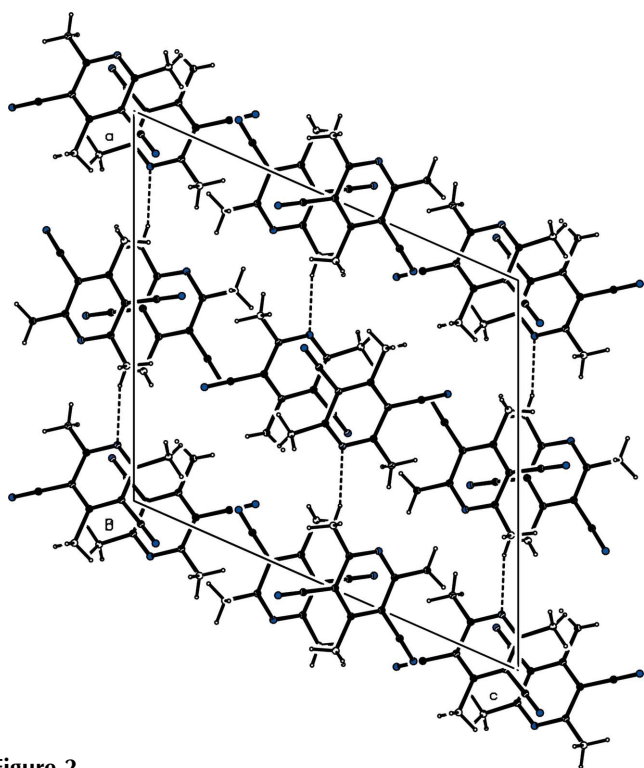


Figure 2
Crystal packing of (I), viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

unit consists of two molecules. The high degree of planarity suggests that the excellent electron-withdrawing power of (I) arises from the cumulative effects of the two cyano groups on the pyridine ring. The C6–N2 and C8–N3 bonds (Table 1) are slightly shorter than C4–N1 of the pyridine ring, possibly because of the extensive conjugation effects in (I). All other bond lengths and angles in (I) are within their normal ranges. In the crystal structure of (I), weak C19–H19···N1 interactions occur (Table 2), linking the molecules into chains propagating along [101] (Fig. 2).

Experimental

3,5-Dibromo-2,4,6-trimethylpyridine was synthesized according to a literature procedure (Attias *et al.*, 2002). *N,N*-dimethylformamide

was dried and distilled over CaH₂ before use. Copper cyanide was used as received without further purification. 3,5-Dibromo-2,4,6-trimethylpyridine (12.8 g, 0.045 mol), copper cyanide (10 g, 0.142 g), and DMF (40 ml) were refluxed for 6 h with stirring. The reaction mixture was poured, while stirring, into 400 ml of cold water. The resulting precipitate was collected and washed successively with water, warm aqueous sodium cyanide (10%, 150 ml), and then water. The resulting brown product was extracted four times with dichloromethane. Finally, after the removal of the solvent, 6.18 g (0.036 mol) of 3,5-dicyano-2,4,6-trimethylpyridine was obtained as a brown powder (yield: 79%). Crystals suitable for X-ray diffraction were obtained by sublimation of (I) under reduced pressure, and colourless crystals of (I) were collected.

Crystal data

C ₁₀ H ₉ N ₃	<i>Z</i> = 8
<i>M_r</i> = 171.20	<i>D_x</i> = 1.208 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 15.4261 (17) Å	<i>μ</i> = 0.08 mm ⁻¹
<i>b</i> = 8.0266 (9) Å	<i>T</i> = 292 (2) K
<i>c</i> = 16.6153 (19) Å	Block, colourless
<i>β</i> = 113.802 (2)°	0.30 × 0.20 × 0.10 mm
<i>V</i> = 1882.3 (4) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	19228 measured reflections
<i>φ</i> and <i>ω</i> scans	4297 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2170 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.978, <i>T</i> _{max} = 0.992	<i>R</i> _{int} = 0.097
	<i>θ</i> _{max} = 27.5°

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.059	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0795 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.164	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>S</i> = 0.90	(Δ/ <i>σ</i>) _{max} = 0.034
4297 reflections	Δ <i>ρ</i> _{max} = 0.21 e Å ⁻³
241 parameters	Δ <i>ρ</i> _{min} = -0.18 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

C2–C7	1.499 (3)	C6–N2	1.139 (3)
C4–N1	1.333 (2)	C8–N3	1.136 (3)
C4–C9	1.497 (3)		
C4–N1–C5	119.62 (16)	C15–N4–C14	119.28 (17)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C19–H19A···N1	0.96	2.58	3.510 (3)	164
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All H atoms were placed in geometrically idealized positions (C–H = 0.96 Å) and refined as riding, with *U*_{iso}(H) = 1.5*U*_{eq}(C).

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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