

3-Phenyl-1,5-di-2-pyridylpentane-1,5-dione

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Key indicators

Single-crystal X-ray study
 $T = 150\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.041
 wR factor = 0.111
 Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_2$, shows both π - π stacking of the pyridine groups and significant $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonding.

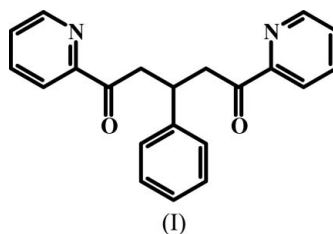
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Comment

2,2':6',2''-Terpyridine and its derivatives have been widely used for complexation of transition metals (Gao *et al.*, 2003; Sharma *et al.*, 2005). In more recent times there has been a lot of interest in these ligands as synthetic building blocks for supramolecular structures (Hofmeier & Schubert, 2004). Multistep syntheses (Kröhnke, 1976; Collin *et al.*, 1996), as well as single-step approaches for these ligands, have been developed (Tu *et al.*, 2005).

The title compound, (I), is a synthetic intermediate for the compound 4'-phenyl-2,2':6',2''-terpyridine. The synthesis and characterization of the latter have been described previously along with other derivatives (Constable *et al.*, 1990; Moya *et al.*, 2001). The structure of the fluorinated analogue, 3-(4-fluorophenyl)pentane-1,5-bis(2-pyridyl)-1,5-dione, (II), has been reported previously (Constable *et al.*, 1998). A search of the CSD (Version 5.27) showed that no other members of this family have been structurally characterized (Allen, 2002; Fletcher *et al.*, 1996).



The structure of (I) is shown in Fig. 1. The mean planes of the two pyridine rings are inclined at $11.26(7)^\circ$. The phenyl ring, comprising C16–C21, is inclined by $87.08(3)^\circ$ to the mean plane of the rest of the molecule. The fluorinated analogue (II) is essentially isomorphous with the present compound, the fluorinated phenyl group making no significant difference to the molecular packing. Constable *et al.* (1998) stated that there were neither stacking interactions nor significant short intermolecular contacts in the crystal structure of (II). We have perhaps taken a more liberal view, and observed both π - π stacking and $\text{C}-\text{H}\cdots\text{O}/\text{N}$ hydrogen bonding in (I).

Fig. 2 shows a packing diagram, viewed perpendicular to the a axis and illustrates the π - π stacking of the pyridine rings, in which rings comprising N1/C1–C5 alternate with those comprising N2/C11–C15. As mentioned above, the rings are

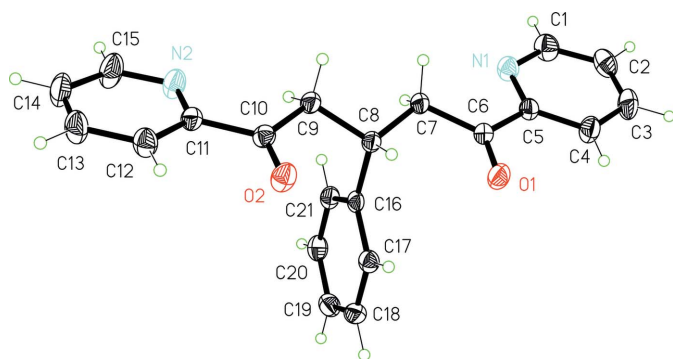


Figure 1
The molecular structure of (I); displacement ellipsoids are drawn at the 50% probability level.

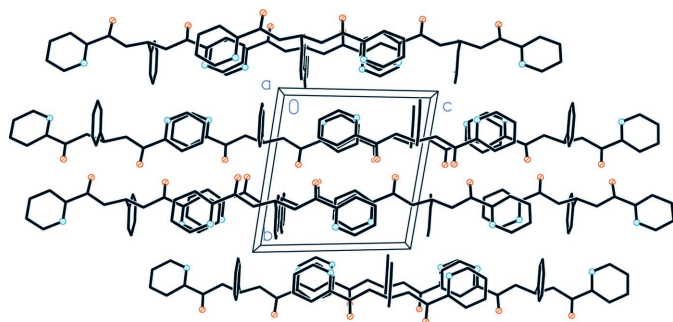


Figure 2
Packing diagram viewed down the *a* axis and showing π - π stacking. H atoms have been omitted for clarity.

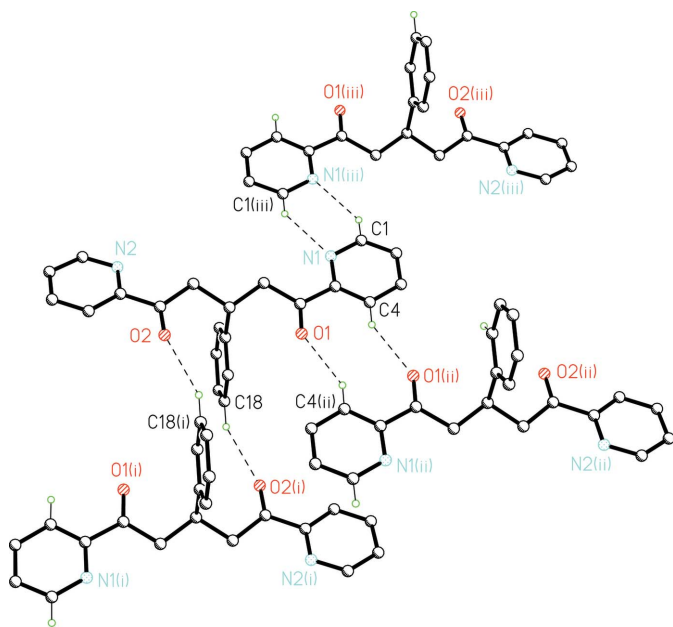


Figure 3
Intermolecular C—H...O and C—H...N hydrogen bonding (dashed lines). H atoms not involved in hydrogen bonding have been omitted for clarity. Symmetry codes as in Table 1.

inclined at $11.26(7)^\circ$; the centroid-centroid distance is 3.907 \AA and the centroid of the N1/C1–C5 ring is $3.684(1) \text{ \AA}$

from the mean plane of the N2/C11–C15 ring under symmetry operation $(-1 + x, y, -1 + z)$.

Three sets of intermolecular hydrogen-bonding interactions are shown in Fig. 3 and listed in Table 1. Each of the interactions is paired by symmetry, giving rise to cyclic patterns which can be described as $R_2^2(16)$, $R_2^2(10)$ and $R_2^2(6)$ for C18—H18...O2ⁱ, C4—H4...O1ⁱⁱ and C1—H1...N1ⁱⁱⁱ, respectively (Etter *et al.*, 1990). The $D \cdots A$ distances and $D-H \cdots A$ angles in these interactions are within the ranges generally observed for such weak hydrogen bonds (Desiraju & Steiner, 1999) and, collectively, they are likely to be responsible for the observed packing.

Experimental

Compound (I) was synthesized as previously reported (Cave & Raston, 2001). The product was recrystallized at room temperature from a methanol–chloroform (1:1) mixture, yielding colourless crystals (m.p. 422–424 K).

Crystal data

$C_{21}H_{18}N_2O_2$
 $M_r = 330.37$
Triclinic, $P\bar{1}$
 $a = 8.3545(5) \text{ \AA}$
 $b = 10.3696(7) \text{ \AA}$
 $c = 10.6370(7) \text{ \AA}$
 $\alpha = 95.208(1)^\circ$
 $\beta = 110.924(1)^\circ$
 $\gamma = 99.762(1)^\circ$

$V = 836.74(9) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.311 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 150(2) \text{ K}$
Block, colourless
 $0.45 \times 0.42 \times 0.17 \text{ mm}$

Data collection

Bruker SMART APEX-II CCD diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.963$, $T_{\max} = 0.986$

8223 measured reflections
3832 independent reflections
3149 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.111$
 $S = 1.09$
3832 reflections
226 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.1695P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C18—H18...O2 ⁱ	0.95	2.62	3.4913 (15)	153
C4—H4...O1 ⁱⁱ	0.95	2.42	3.2556 (16)	146
C1—H1...N1 ⁱⁱⁱ	0.95	2.64	3.4588 (18)	145

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

H atoms bonded to C and N were inserted at calculated positions and refined using a riding model. The constrained distances were 0.95, 0.99 and 1.00 \AA for aryl, methylene and tertiary H atoms, respectively. They were assigned $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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