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3,3′-(Quinoxaline-2,3-diyldimethylene)-bis(pentane-2,4-dione)

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Key indicators

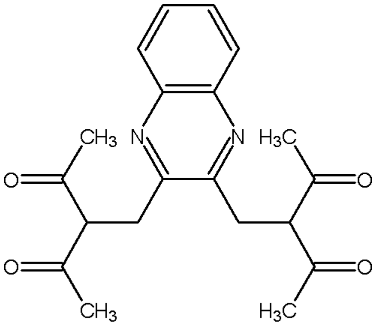
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.116
Data-to-parameter ratio = 17.3

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

In the title compound, $C_{20}H_{24}N_2O_4$, the quinoxalinediyl bridging group separates two β-diketone groups, which are found to be in a pseudo-*trans* configuration. The major contributing packing forces are π–π interactions and weak but influential C—H···O hydrogen bonds.

Comment

We are interested in the synthesis of new bis-β-diketones (H_2L) for the preparation of metallo-supramolecular assemblies. To date, there have been only a few reports concerning structural studies of metal complexes with tetraketones. Examples include binuclear species allowing for selective intramolecular binding, and fascinating triple helicates (Maverick *et al.*, 1990; Clegg *et al.*, 2005; Grillo *et al.*, 1997). We present here the crystal structure of the title compound, (I).



(I)

Compound (I) comprises β-diketone groups separated by a quinoxalinediyl bridging group (Fig. 1). Diketone groups can

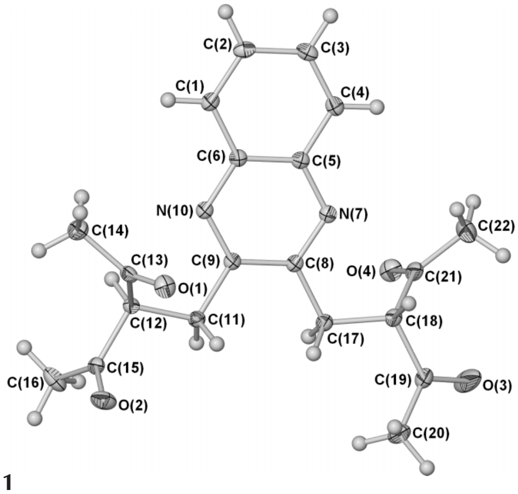


Figure 1
The molecular structure of (I), with the atom-labelling scheme and 50% probability ellipsoids.

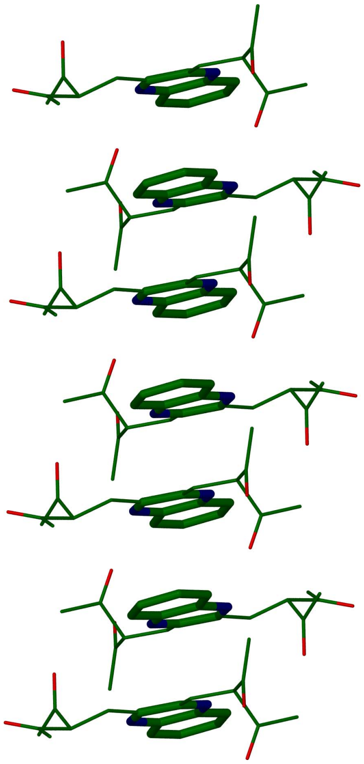


Figure 2
A view of the offset π–π stacking of molecules of (I), to form strands. H atoms have been omitted.

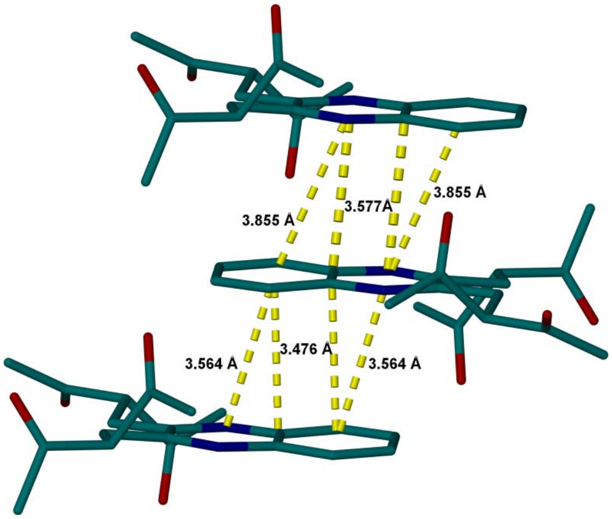


Figure 3
A capped stick representation, showing the π–π stacking geometry of (I). The upper and lower molecules are related to the central one by the symmetry operations $(1 - x, 1 - y, -z)$ and $(1 - x, -y, -z)$, respectively. H atoms have been omitted.

sometimes be found in the tautomeric enol form in tetraketone type molecules (Clegg *et al.*, 2005; Soldatov *et al.*, 2003). This is due to electron delocalization stabilized by hydrogen bonding. The enol form is not found in the case of (I), where weak packing forces cause the diketone groups to adopt a non-parallel orientation. The keto tautomer also persists entirely in solution, as inferred from the ^{1}H NMR spectrum.

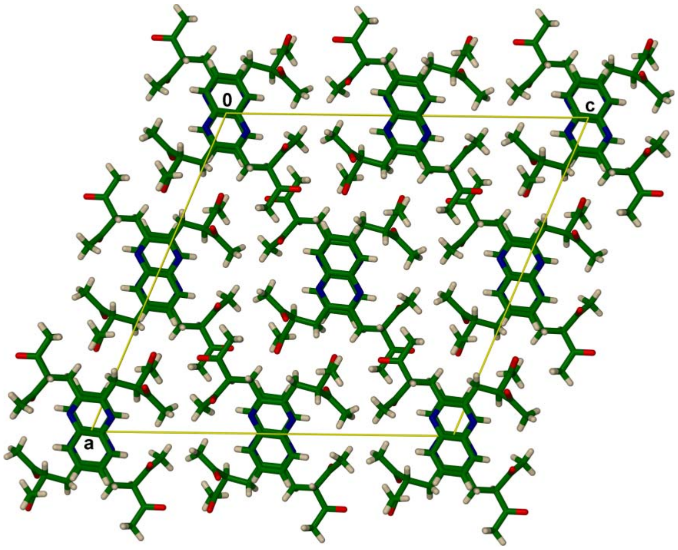


Figure 4
A packing diagram of (I), viewed along [010].

Owing to electron delocalization, the two C=O bonds of the diketone groups of β-diketone ligands must be parallel when complexed to metals. In compound (I), the diketone unit containing atoms O1 and O2 is non-planar, with an O1—C13—C15—O2 torsion angle of 28.8 (1)°. However, the second diketone group, containing atoms O3 and O4, is significantly more distorted from planarity, with an O3—C19—C21—O4 torsion angle of 78.6 (1)°. This type of configuration may not necessarily interfere with metal complexation, as the ligand is very flexible and the distortions described above can be due to packing efficiency and not conformational energy constraints.

Offset π–π stacking of the quinoxalinediyl groups is the major packing force interaction in (I) (Fig. 2). Fig. 3 shows the two types of π–π interactions along the π–π strand, with centroid-to-C—C distances of 3.476 and 3.577 Å, and centroid-to-centroid distances of 3.564 and 3.855 Å. The non-parallel mode of the diketone groups is possibly due to weak C—H···O hydrogen bonds. The shortest of these C—H···O hydrogen bonds involves the least parallel diketone group and has a donor-to-acceptor distance of 3.242 (2) Å, which is longer than the sum of the van der Waals radii of O and C (approximately 3.2 Å; Bondi, 1964). The approximate strengths of the other C—H···O bonds, as inferred by the sum of the van der Waals radii of the appropriate O and C atoms, are all found to be very low and therefore almost insignificant. Therefore, other than π–π stacking of the molecules, the packing of (I) appears to be stabilized by van der Waals interactions (Fig. 4).

Experimental

The synthesis of (I) was carried out using inert-atmosphere techniques and was based on the general method of Martin *et al.* (1959). Acetylacetone (9 mmol) was added slowly to a refluxing solution (368 K) of potassium *tert*-butoxide (6 mmol) in *tert*-butanol. After further refluxing for 10 min, 2,3-bis(bromomethyl)quinoxaline

(3 mmol) was added in small portions. After a further interval of 45 min, KI (*ca* 0.75 mmol) was added. The reaction mixture was stirred and heated at 373 K until moist litmus indicated acidity (5 d). The majority of the *tert*-butanol was removed by distillation. The residue was extracted with water and CH_2Cl_2. The CH_2Cl_2 layer was dried over Na_2SO_4 and the solvent evaporated. Excess acetylacetone was removed from the product under vacuum. After recrystallization from a mixture of CH_2Cl_2 and toluene (1:1), colourless needles of (I) were obtained in 25% yield (m.p. 392–394 K).

Crystal data

$C_{20}H_{22}N_2O_4$
$M_r = 354.41$
Monoclinic, $C2/c$
$a = 22.3830$ (17) Å
$b = 7.4043$ (6) Å
$c = 23.3675$ (18) Å
$\beta = 112.224$ (1)°
$V = 3585.0$ (5) Å^3
$Z = 8$

$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3362 reflections
$\theta = 2.9$–27.8°
$\mu = 0.09$ mm^{-1}
$T = 100$ (2) K
Needle, colourless
0.18 × 0.08 × 0.07 mm

Data collection

Bruker APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.944$, $T_{\max} = 0.994$
10931 measured reflections

4138 independent reflections
3320 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 28.3°$
$h = -28 \rightarrow 28$
$k = -9 \rightarrow 9$
$l = -28 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.117$
$S = 1.00$
4138 reflections
239 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0706P)^2 + 1.0823P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.008$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}

All H atoms were positioned geometrically (C—H = 0.98 and 0.99 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Atwood & Barbour, 2003; Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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