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rac-5-Acetyl-6-(4-nitrophenyl)-6,7-dihydro-5*H*-1,3-dioxolo[4,5-*g*]quinoline-8-one: chains of rings built from C—H···O and C—H···π(arene) hydrogen bonds

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Molecules of the title compound, $C_{18}H_{14}N_2O_6$, are linked into chains by a combination of one C—H···O and one C—H···π(arene) hydrogen bond, augmented by a dipolar carbonyl–carbonyl interaction.

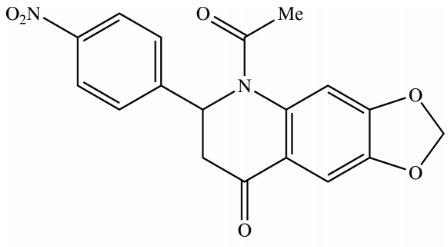
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.041
wR factor = 0.086
Data-to-parameter ratio = 7.4

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

Comment

The title compound, (I), was prepared as an intermediate in the preparation of new bis-amides derived from tetrahydroquinolones, for use as model compounds for DNA intercalating agents (Gamage *et al.*, 1999; Chacón-García & Martínez, 2001; Deady *et al.*, 2001).



(I)

Compound (I) (Fig. 1) crystallizes in the polar space group $Pna2_1$. The molecule contains a stereogenic centre at C6, and the selected reference molecule is of S configuration; however, the space group accommodates equal numbers of R and S enantiomers.

For the heterocyclic ring (N5/C4A/C8A/C8/C7/C6), the ring-puckering parameters (Cremer & Pople, 1975) for this atom sequence, θ = 124.7 (3)° and φ = 120.3 (4)°, indicate an almost pure envelope form (Evans & Boeyens, 1989). The inter-bond angles at N5 (Table 1) indicate that this atom has

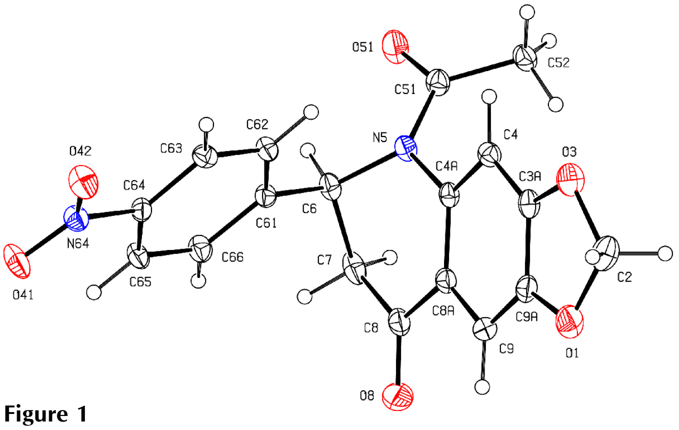


Figure 1
The S enantiomer of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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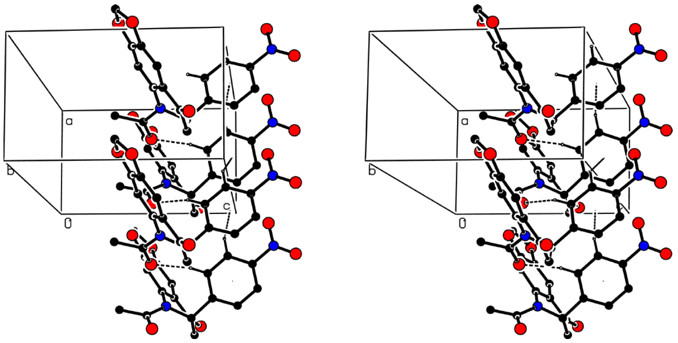

Figure 2
Stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain along [100].

effectively planar coordination, as expected for amidic N, but, unexpectedly, the nitrophenyl substituent at C6 occupies an axial site. Within the fused-ring system, the bond lengths (Table 1) show several unexpected features. In particular, the bonds C3A—C4 and C9—C9A are significantly shorter than the other bonds in the carbocyclic aromatic ring, and the bond C4A—N5 is very long for its type: the mean value for bonds of this type (Allen *et al.*, 1987) is 1.371 Å. It may also be noted that the two carbonyl C═O distances are identical, despite their different local environments.

The molecules of (I) are linked into chains by a combination of C—H···O and C—H···π(arene) hydrogen bonds, augmented by a dipolar carbonyl–carbonyl interaction. Atoms C62 and C63 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors, respectively, to amidic atom O51 and to the ring C61—C66, both in the molecule at ($\frac{1}{2}+x$, $\frac{3}{2}-y$, z), and propagation of these interactions produces a chain of rings running parallel to the [100] direction and generated by the *a* glide plane at $y = 0.75$ (Fig. 2). In addition, carbonyl atom O51 in the molecule at (*x*, *y*, *z*) forms a short contact with the carbonyl atom C51 in the molecule at ($x-\frac{1}{2}$, $\frac{3}{2}-y$, z): the O···C distance is 3.001 (3) Å, the C—O···C angle is 150 (4)° and the O···C—O angle is 87.4 (2)°, indicative of a type I interaction (Allen *et al.*, 1998), which reinforces the [100] chain.

Two antiparallel chains of this type pass through each unit cell, generated by the *a* glide planes at $y = 0.25$ and 0.75, but there are no direction-specific interactions between adjacent chains. In particular, there are no π–π stacking interaction and no C—H···O hydrogen bonds involving the nitro O atoms.

Experimental

A mixture of 6-(4-nitrophenyl)-6,7-dihydro-5*H*-[1,3]dioxolo[4,5-*g*]quinolin-8-one (250 mg, 0.71 mmol) (Donnelly & Farell, 1990) and acetic anhydride (3 ml) was heated at 353 K for 90 min. After reaction was complete (as shown by thin-layer chromatography), the solvent was removed under vacuum and the resulting solid was washed with water and then purified by column chromatography on silica gel with chloroform–ethyl acetate (9:1 *v*/*v*) as eluant, to give a pale yellow solid (60% yield, m.p. 483 K). MS (70 eV): *m*/*e* (%) 354 (40, M^+), 312 (86), 190 (39), 43 (100). Crystals suitable for single-crystal X-ray diffraction were grown from a solution in 96% aqueous ethanol.

Crystal data

$C_{18}H_{14}N_2O_6$
$M_r = 354.31$
Orthorhombic, $Pna2_1$
$a = 6.5253$ (2) Å
$b = 21.4286$ (5) Å
$c = 10.8198$ (9) Å
$V = 1512.91$ (14) Å^3
$Z = 4$
$D_x = 1.556$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1952 reflections
$\theta = 3.3$–27.1°
$\mu = 0.12$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.30 × 0.10 × 0.09 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.956$, $T_{\max} = 0.989$
15335 measured reflections
1762 independent reflections

1360 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\max} = 27.1°$
$h = -8 \rightarrow 7$
$k = -27 \rightarrow 27$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.087$
$S = 1.06$
1762 reflections
237 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.0405P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0110 (18)

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.431 (4)	C8—C8A	1.480 (4)
C2—O3	1.440 (4)	C8A—C9	1.407 (4)
O3—C3A	1.367 (3)	C9—C9A	1.352 (4)
C3A—C4	1.369 (4)	C9A—O1	1.381 (3)
C4—C4A	1.400 (4)	C3A—C9A	1.385 (4)
C4A—N5	1.425 (3)	C4A—C8A	1.403 (4)
N5—C6	1.472 (4)	N5—C51	1.388 (4)
C6—C7	1.527 (4)	C51—O51	1.223 (3)
C7—C8	1.506 (4)	C8—O8	1.223 (4)
C51—N5—C4A	125.0 (2)	C4A—N5—C6	115.1 (2)
C51—N5—C6	118.1 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C62—H62···O51$^{\rm i}$	0.95	2.48	3.358 (4)	153
C63—H63···*Cg*1$^{\rm i}$	0.95	2.98	3.693 (3)	132

Symmetry code: (i) $\frac{1}{2}+x, \frac{3}{2}-y, z$. *Cg*1 is the centroid of ring C61–C66

All H atoms were located in difference maps and subsequently treated as riding atoms, with distances C—H = 0.95 (aromatic), 0.98 (methyl), 0.99 (CH_2) or 1.00 Å (aliphatic CH), and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, or $1.5U_{\rm eq}({\rm C})$ for the methyl group. The value of the Flack parameter [0.2 (13); Flack, 1983] was indeterminate (Flack & Bernardinelli, 2000), and hence the correct orientation of the structure relative to the polar axis direction could not be established (Jones, 1986). Accordingly, the Friedel-equivalent reflections were merged prior to the final refinement.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997);

program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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