

2,6-Bis(butylamino)-4,8-dihydroxy-1,5-naphthalenedione

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Key indicators

Single-crystal X-ray study

 $T = 93\text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$ R factor = 0.047 wR factor = 0.117

Data-to-parameter ratio = 12.7

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

The title compound, $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_4$, is an aminonaphthoquinone derivative that exhibits a large third-order non-linear optical susceptibility. The centrosymmetric naphthoquinone moieties are connected by bifurcated $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form a ribbon structure along $[\bar{1}10]$. The molecules are stacked along the c axis, with overlap occurring only at the periphery of the naphthoquinone skeleton.

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Comment

The title compound, (I), is an aminonaphthoquinone derivative; these are of great interest as dyestuffs and as materials for biological and pharmaceutical applications (Patai, 1974). These derivatives are characterized by intra- and intermolecular hydrogen bonds, accompanied by a large bathochromic shift upon crystallization. A large third-order NLO (non-linear optical) susceptibility of (I) has been reported (Matsuoka *et al.*, 1995; Kim *et al.*, 1998). The present structure analysis has been carried out as part of the above investigation to study the correlation between the crystal structure and the NLO properties.

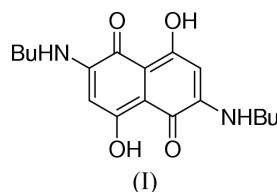


Fig. 1 shows the molecular structure of (I). The naphthoquinone skeleton is centrosymmetric and entirely planar; the *n*-butyl chains extend from it, almost vertically, in a zigzag fashion (Table 1). As is apparent from Fig. 2, there are intra- and intermolecular hydrogen bonds (Table 2). The naphthoquinone moieties are connected by $\text{N}-\text{H}\cdots\text{O}$ bifurcated hydrogen bonds to form a ribbon structure along $[\bar{1}10]$.

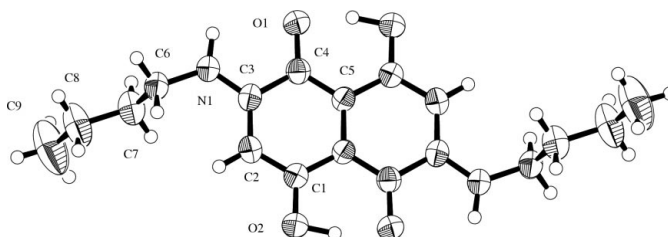


Figure 1

A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms.

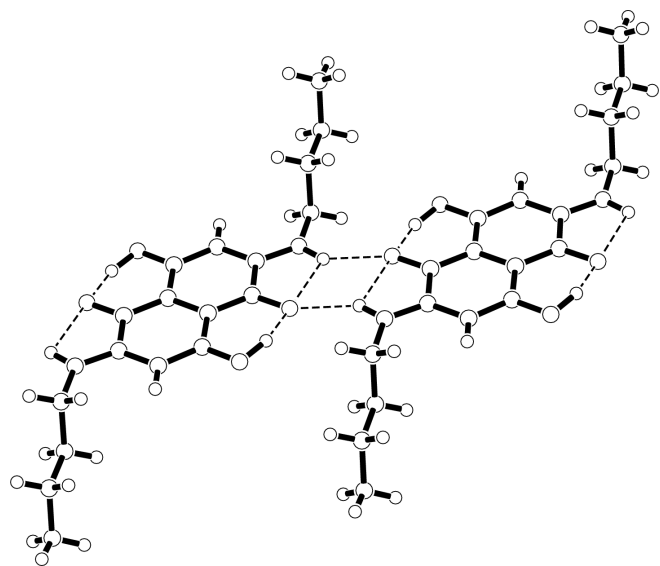


Figure 2
Molecular arrangement projected on to the naphthoquinone plane, showing intra- and intermolecular hydrogen bonds in broken lines.

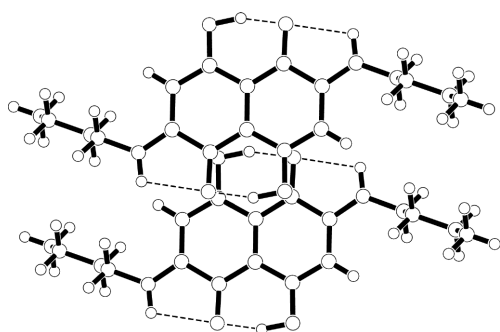


Figure 3
Overlap between the two molecules along the stacking *c* axis, showing some close atomic contacts.

The molecules are stacked along the *c* axis, with little overlap of the naphthoquinone skeleton; in Fig. 3, the upper molecule is depicted pointing slightly left-ward relative to the lower molecule. It should be noted that some close atomic contacts are recognized; these occur only at the periphery of the molecule. The carbonyl O atom of the upper molecule is directly over the C atom bonded to the hydroxy group of the lower molecule, whereas the carbonyl C atom of the upper molecule is directly over the O atom of the hydroxy group of the lower molecule. The same atomic overlap also occurs at another pair of carbonyl and hydroxy groups. The short contact distances are 3.354 (2) and 3.341 (2) Å for C1 \cdots O1(*x* - 1, *y*, *z*) and O2 \cdots C4(*x* + 1, *y*, *z*), respectively. These close atomic contacts suggest the existence of relatively strong π - π interactions along the stacking *c* axis.

Experimental

The title compound, (I), was synthesized by amination of naphthazarin with *n*-butylamine in the presence of cuprous chloride (Kim *et al.*, 1996). Single crystals of (I) were grown from a mixed solvent of

benzene and methylene chloride, giving rise to lustrous crystals with a platelet form.

Crystal data

$C_{18}H_{24}N_2O_4$	<i>Z</i> = 1
$M_r = 332.40$	$D_x = 1.275 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 5.2257(7) \text{ \AA}$	Cell parameters from 3066 reflections
$b = 6.8930(9) \text{ \AA}$	$\theta = 3.7\text{--}68.1^\circ$
$c = 12.162(1) \text{ \AA}$	$\mu = 0.74 \text{ mm}^{-1}$
$\alpha = 97.72(1)^\circ$	$T = 93.2 \text{ K}$
$\beta = 91.93(1)^\circ$	Platelet, black
$\gamma = 93.66(1)^\circ$	$0.35 \times 0.20 \times 0.03 \text{ mm}$
$V = 432.83(9) \text{ \AA}^3$	

Data collection

Rigaku R-Axis RAPID imaging-plate diffractometer	1429 independent reflections
ω scans	775 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (Higashi, 1995)	$R_{\text{int}} = 0.038$
$T_{\text{min}} = 0.738$, $T_{\text{max}} = 0.978$	$\theta_{\text{max}} = 68.2^\circ$
3858 measured reflections	$h = -6 \rightarrow 6$
	$k = -8 \rightarrow 8$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.05[\text{Max}(F_o^2, 0) + 2F_c^2]/3)^2]$
$wR(F^2) = 0.117$	$(\Delta/\sigma)_{\text{max}} = 0.016$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
1421 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
112 parameters	

Table 1

Selected geometric parameters (Å, °).

O1—C4	1.292 (2)	C3—C4	1.474 (3)
O2—C1	1.334 (2)	C4—C5	1.396 (3)
N1—C3	1.334 (2)	C5—C5 ⁱ	1.421 (4)
N1—C6	1.447 (3)	C6—C7	1.509 (3)
C1—C2	1.388 (3)	C7—C8	1.509 (3)
C1—C5 ⁱ	1.426 (3)	C8—C9	1.487 (4)
C2—C3	1.395 (3)		
C3—N1—C6	125.8 (2)	O1—C4—C5	123.3 (2)
O2—C1—C2	118.6 (2)	C3—C4—C5	118.5 (2)
O2—C1—C5 ⁱ	119.7 (2)	C1 ⁱ —C5—C4	120.2 (2)
C2—C1—C5 ⁱ	121.7 (2)	C1 ⁱ —C5—C5 ⁱ	118.5 (2)
C1—C2—C3	120.1 (2)	C4—C5—C5 ⁱ	121.3 (2)
N1—C3—C2	124.4 (2)	N1—C6—C7	113.6 (2)
N1—C3—C4	115.7 (2)	C6—C7—C8	112.3 (2)
C2—C3—C4	119.9 (2)	C7—C8—C9	114.9 (2)
O1—C4—C3	118.2 (2)		

Symmetry code: (i) 1 - *x*, 1 - *y*, 2 - *z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H1 \cdots O1 ⁱ	1.06	1.49	2.517 (2)	161
N1—H3 \cdots O1	0.95	2.24	2.664 (2)	106
N1—H3 \cdots O1 ⁱⁱ	0.95	2.04	2.871 (2)	146

Symmetry codes: (i) 1 - *x*, 1 - *y*, 2 - *z*; (ii) -*x*, 2 - *y*, 2 - *z*.

The hydroxy H atom was found in a difference Fourier map but not refined (O—H = 1.059 Å). All other H atoms were positioned geometrically and not refined [C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$].

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure:

SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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