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4,8-Bis[(4-butylphenyl)amino]-1,5-naphthalenedione

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.097
wR factor = 0.209
Data-to-parameter ratio = 11.4

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

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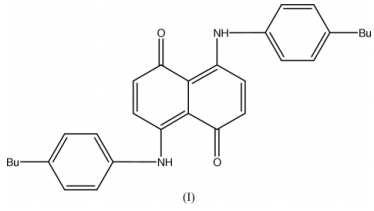
The title compound, $C_{30}H_{32}N_2O_2$, is an aminonaphthoquinone derivative that exhibits a third-order non-linear optical susceptibility. The centrosymmetric aminonaphthoquinone moieties are connected by bifurcated N—H···O hydrogen bonds to form a ribbon structure along the *c* axis. The molecules are stacked along the *a* axis, with overlap occurring only at the periphery of the naphthoquinone skeleton.

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.



(I)

Fig. 1 shows the molecular structure of (I). The naphthoquinone skeleton is centrosymmetric and entirely planar; it makes a dihedral angle of 63.4 (1)° (Table 1) with each substituted phenyl ring. The *n*-butyl chain is almost vertically extended, in a zigzag fashion, from the benzene ring. As is apparent from Fig. 2, there are intra- and intermolecular hydrogen bonds (Table 2). The aminonaphthoquinone moieties are connected by these bifurcated hydrogen bonds to form a ribbon structure along the *c* axis. There exists a small step between the hydrogen-bonded molecular planes; the molecule on the right in Fig. 2 is located slightly higher than that on the left (by *ca* 1 Å).

The molecules are stacked along the *a* axis, with overlap occurring only at the periphery of the naphthoquinone skeleton. The close contacts are C2···C2^{iii} [3.609 (6) Å; symmetry code (iii): $x+1, y, z$] and C2···C3^{iii} [3.758 (6) Å].

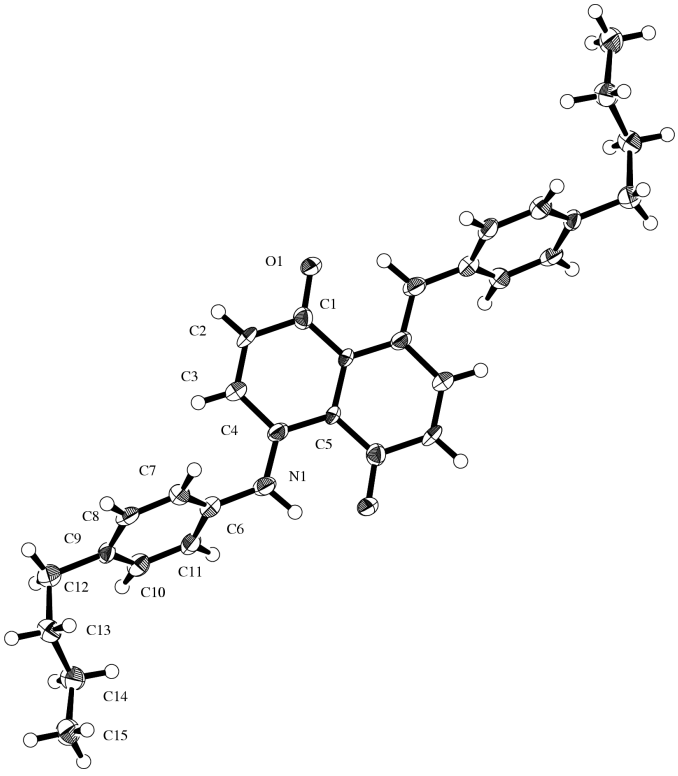


Figure 1
A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms.

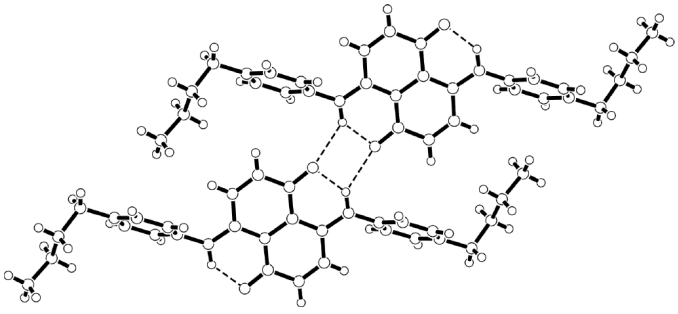


Figure 2
Molecular arrangement projected on to the aminonaphthoquinone plane, showing intra- and intermolecular hydrogen bonds as broken lines.

Experimental

The title compound, (I), was prepared by copper-catalysed amination of naphthazarin with 4-*n*-butylaniline in the presence of cuprous chloride (Kim *et al.*, 1996). Single crystals of (I) were grown from a 1:1 mixed solvent of methylene chloride and cyclohexane. The single crystals were lustrous platelets, but slightly curved.

Crystal data

$C_{30}H_{32}N_2O_2$
M_r = 452.60
Triclinic, $P\overline{1}$
a = 6.582 (5) Å
b = 11.377 (5) Å
c = 8.236 (4) Å
α = 85.46 (5)°
β = 76.18 (4)°
γ = 89.29 (5)°
V = 597.0 (6) Å^3
Z = 1
D_x = 1.259 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 3798 reflections
θ = 3.9–68.0°
μ = 0.62 mm^{-1}
T = 296.2 K
Needle, black
0.35 × 0.06 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (Higashi, 1995)
T_{min} = 0.566, T_{max} = 0.988
4848 measured reflections
1885 independent reflections
1104 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.097
θ_{max} = 68.0°
$h = -6 \rightarrow 6$
$k = -13 \rightarrow 13$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$= 0.097
$wR(F^2)$ = 0.209
S = 1.55
1759 reflections
154 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.045[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3)^2]$
$(\Delta/\sigma)_{max}$ = 0.010
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.286 (4)	C4—C5	1.401 (4)
N1—C4	1.362 (4)	C5—C5^{i}	1.445 (6)
N1—C6	1.421 (4)	C9—C12	1.519 (5)
C1—C2	1.444 (5)	C12—C13	1.546 (5)
C1—C5^{i}	1.433 (4)	C13—C14	1.529 (5)
C2—C3	1.350 (5)	C14—C15	1.527 (5)
C3—C4	1.438 (4)		
C4—N1—C6	125.6 (3)	C1^{i}—C5—C5^{i}	119.0 (4)
O1—C1—C2	118.1 (3)	C4—C5—C5^{i}	121.1 (4)
O1—C1—C5^{i}	123.4 (3)	N1—C6—C7	122.2 (3)
C2—C1—C5^{i}	118.5 (3)	N1—C6—C11	118.0 (3)
C1—C2—C3	120.9 (3)	C8—C9—C12	119.1 (3)
C2—C3—C4	122.5 (3)	C10—C9—C12	123.0 (3)
N1—C4—C3	120.0 (3)	C9—C12—C13	112.7 (3)
N1—C4—C5	121.9 (3)	C12—C13—C14	113.3 (3)
C3—C4—C5	118.0 (3)	C13—C14—C15	110.8 (3)
C1^{i}—C5—C4	119.9 (3)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H3···O1^{i}	0.95	1.82	2.572 (4)	134
N1—H3···O1^{ii}	0.95	2.43	3.077 (4)	125

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

All H atoms were positioned geometrically [C—H = 0.95 Å and U_{iso} = 1.2 times U_{eq}(C)] and not refined. Since the single crystal of the platelet was slightly curved, the final R factor remained rather high.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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