

2-(Cyclohexylamino)-1,4-naphthoquinone

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Key indicators

 Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
 R factor = 0.049
 wR factor = 0.136
 Data-to-parameter ratio = 17.1

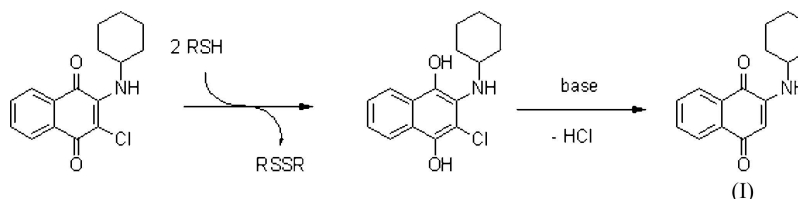
 For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

 The molecules of the title compound, $\text{C}_{16}\text{H}_{17}\text{NO}_2$, interact by
 π - π stacking between the naphthoquinone ring systems.

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Comment

In research focusing on the development of redox-active naphthoquinone-based healing agents we have observed unexpected reactivity of amine-substituted chloronaphthoquinones and we report here a by-product from one of our syntheses. In an attempt to prepare 3-(cyclohexylamino)-2-(*p*-tolylsulfanyl)naphthalene-1,4-dione by reaction of 2-chloro-3-(cyclohexylamino)naphthalene-1,4-dione with thiocresol under basic conditions, we isolated the title compound, (I), in modest yield. We postulate that the dechlorinated product was obtained *via* a quinolic intermediate obtained after oxidation of thiocresol to the corresponding disulfide. The reduction of chloronaphthoquinones has been described before (Reynolds *et al.*, 1964), but what is unusual here is that a low-potential aminoquinone is acting as an oxidant. Elimination of HCl from the intermediate 2-chloro-3-(cyclohexylamino)naphthalene-1,4-diol would be readily achieved under the basic conditions employed to afford the title compound.

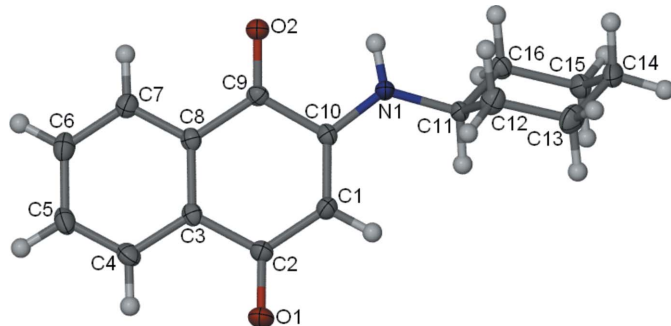


In (I), the naphthoquinone system is substituted with a cyclohexylamino group in position 2 (Fig. 1). The cyclohexyl group is in the chair conformation with an average C—C bond length of 1.496 (2) Å which lies well within the range of classical values. The central C10—N1—C11 angle is 126.73 (12)°, a value which is slightly more obtuse than that found in the related compound 3-chloro-2-pyrrolidino-1,4-naphthoquinone (Lynch *et al.*, 2002). An acute intramolecular N—H...O bond (Table 1) helps to establish the molecular conformation of (I).

The molecular packing diagram (Fig. 2) shows the occurrence of centrosymmetric intermolecular π - π stacking of the C1/C2/C3/C8/C9/C10 aromatic ring, with a centroid-centroid distance of 3.8694 (8) Å.

Experimental

3-Chloro-2-(cyclohexylamino)-1,4-naphthoquinone (0.5 g, 1.73 mmol), potassium carbonate (365 mg, 2.64 mmol) and *p*-thioltoluene (241 mg, 2.54 mmol) were reacted in acetonitrile (40 ml). The solu-

**Figure 1**

View of the molecular structure of (I), showing 50% displacement ellipsoids (H atoms are represented by spheres of arbitrary radius).

tion mixture was refluxed overnight under an inert nitrogen atmosphere. This solution was filtered, dried and purified by flash column chromatography (SiO_2) using CHCl_3 as the eluant. The title compound was found at $R_F = 0.36$. Ruby-red blocks of (I) were obtained by slow evaporation of a CHCl_3 solution (yield 185 mg, 42%).

Crystal data

$\text{C}_{16}\text{H}_{17}\text{NO}_2$
 $M_r = 255.31$
 Monoclinic, $P2_1/c$
 $a = 10.3204$ (3) Å
 $b = 6.3380$ (2) Å
 $c = 18.9664$ (7) Å
 $\beta = 96.179$ (1)°
 $V = 1233.40$ (7) Å³

$Z = 4$
 $D_x = 1.375$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 150$ (2) K
 Block, red
 $0.52 \times 0.40 \times 0.22$ mm

Data collection

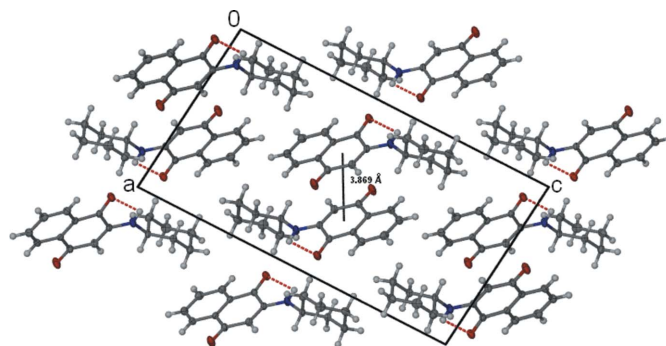
Bruker–Nonius KappaCCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.954$, $T_{\max} = 0.980$

11095 measured reflections
 3094 independent reflections
 2075 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$
 $\theta_{\text{max}} = 28.7^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.136$
 $S = 1.05$
 3094 reflections
 172 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0722P)^2 + 0.0683P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

**Figure 2**

The packing of (I) showing the π - π stacking. The dashed line indicates the intramolecular hydrogen bond.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O2}$	0.88	2.19	2.5917 (16)	107

The H atoms were placed in calculated positions ($\text{C}-\text{H} = 0.95$ – 1.00 and $\text{N}-\text{H} = 0.88$ Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

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