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N,*N*′-Di-1-naphthylurea revisited

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.005 Å
R factor = 0.059
wR factor = 0.150
Data-to-parameter ratio = 7.6

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

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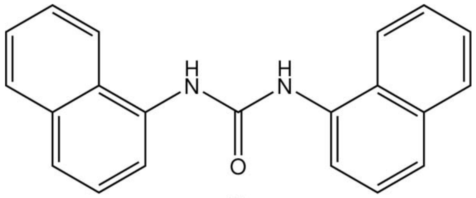
The molecule of the title compound, $C_{21}H_{16}N_2O$, has crystallographic twofold rotation symmetry, with the C═O group lying on the rotation axis. Intermolecular N—H···O hydrogen bonds result in a chain structure containing $R_2^1(6)$ loops. This orthorhombic structure probably represents a correction of a previous study where space group $P2_1$ was found [Kurth & Lewis (2003), *J. Am. Chem. Soc.* **125**, 13760–13767].

Comment

The title compound, (I), arose as an unexpected side-product during our studies of cyclodextrin polymers. Its crystal structure and photophysical properties were recently described by Kurth & Lewis (2003).


(I)

As modelled here in space group $P2_12_12$, the complete molecule of (I) is generated by twofold rotation symmetry, with the central C═O group lying on the rotation axis (Fig. 1). The pendant naphthyl groups adopt a *Z*,*Z* conformation, and the dihedral angle between them is 84.09 (6)°. The dihedral angle between the C1–C10 fused ring system and the C11/O1/N1/N1^{i} [symmetry code: (i) $1 - x$, $1 - y$, z] grouping is 50.27 (11)°. Otherwise, the geometry of (I) is normal (Allen *et al.*, 1987).

In the crystal structure of (I), intermolecuar N—H···O bonds occur (Fig. 2, Table 1), leading to [001] chains containing $R_2^1(6)$ loops (Bernstein *et al.*, 1995). Weak π–π stacking helps to consolidate the [001] chains, with a separa-

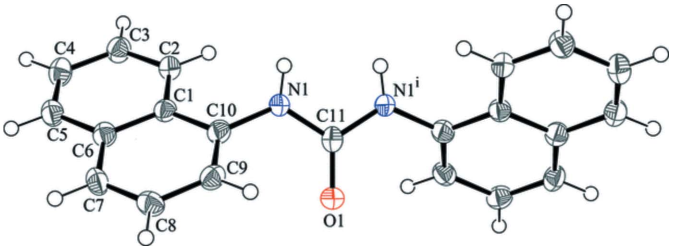


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry code: (i) $1 - x$, $1 - y$, z.]

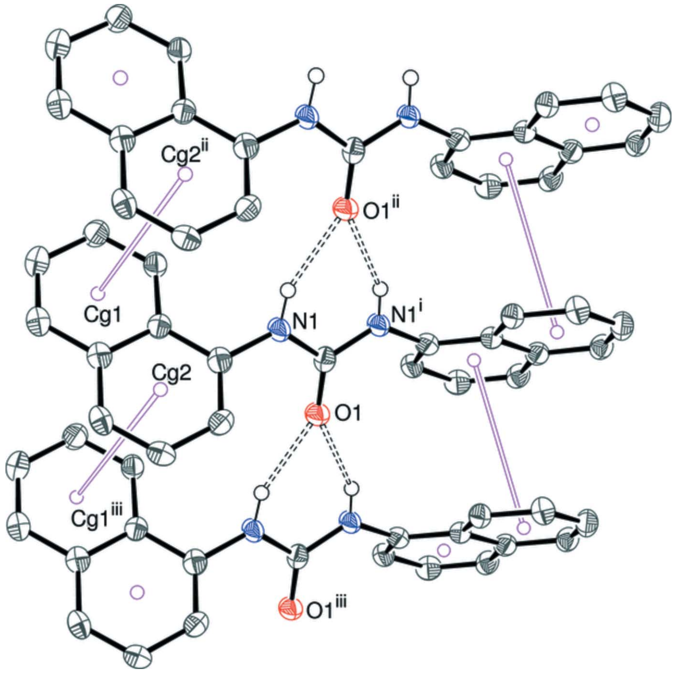


Figure 2
A fragment of an [001] hydrogen-bonded chain of molecules in (I), with all H atoms except H1 omitted for clarity and hydrogen bonds shown as double dashed lines. The π–π stacking interactions are shown as open lines. *Cg*1 is the centroid of the C1–C6 ring and *Cg*2 is the centroid of the C1/C6–C10 ring. [Symmetry codes: (i) $1 - x, 1 - y, z$; (ii) $x, y, z - 1$; (iii) $x, y, z + 1$.]

tion of 3.794 (2) Å between the centroids of the C1–C6 and C1/C6–C10 rings, the latter generated by the symmetry operation ($x, y, z - 1$) (Fig. 2). The 'up' or 'down' sense of the chains with respect to the *c*-axis direction alternates with respect to [110] in the packing of (I) (Fig. 3).

Kurth & Lewis (2003) found a monoclinic unit cell, with a = 4.58 (2), b = 11.27 (3), c = 14.71 (5) Å and β = 91.3 (8)° (space group $P2_1$) in their study of (I). Thin colourless needles were grown from pure dimethyl sulfoxide solution and the crystal quality was poor. In their structure, the molecule of (I) has no crystallographically imposed symetry and the dihedral angle between the naphthalene ring systems is 84.10 (7)° [calculated with *PLATON* (Spek, 2003)].

Becase the molecular conformations are almost identical and the unit cells are clearly related (with the appropriate axis transformations), it seems probable that the present $P2_12_12$ structure of (I) represents a correction of the $P2_1$ monoclinic structure (Fig. 4). The N-bound H atoms were not located by Kurth & Lewis, but it seems highly likely that similar hydrogen-bonded chains are formed to the ones found here. However, as the two materials were crystallized from different solvents by different routes, it is possible that they are real and closely related polymorphs: a *PLATON* symmetry check of the monoclinic structure did not indicate any missed symmetry, perhaps suggesting that some subtle distortions really lower the symmetry from orthorhombic to monoclinic.

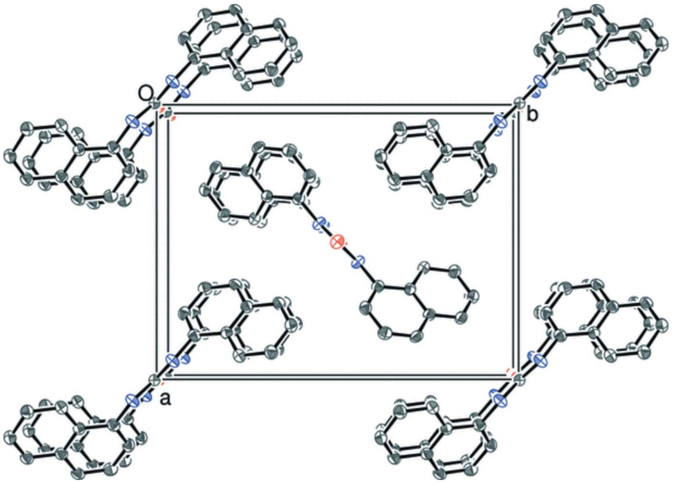


Figure 3
The packing of (I), with all H atoms omitted for clarity, viewed down [001].

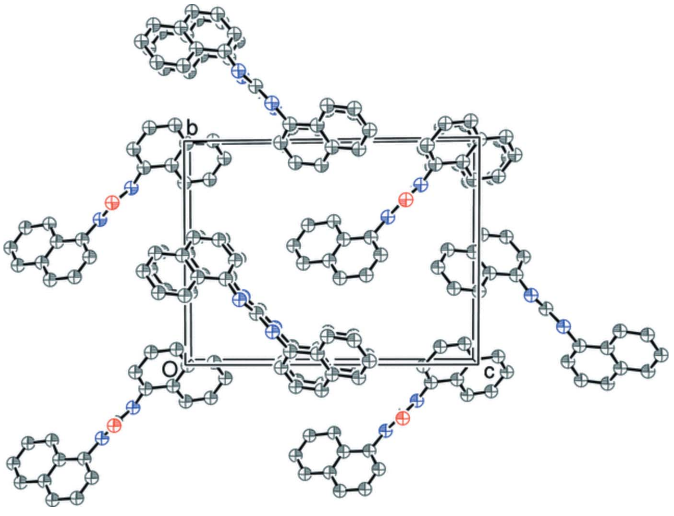


Figure 4
The packing in the monoclinic form of (I), viewed down [100]. Atoms are represented by arbitrary spheres and all H atoms have been omitted for clarity.

Experimental

The title compound arose as a side-product in an attempted polymerization reaction of a naphthylurea-substituted cyclodextrin. β-Cyclodextrin (142 mg, 0.146 mmol) was suspended in dry tetrahydrofuran (THF) and 1-naphthyl isocyanate (592 mg, 3.5 mmol, 24 equivalents) was added. The reaction was heated under reflux in an Ar atmosphere for 24 h and the THF was removed *in vacuo*. The product was refluxed in chloroform (20 ml) for 1 h then gravity-filtered from the solvent to yield 684 mg of crude product. Acetone (75 ml) was added and filtered, and the filtrate dried overnight to yield 619 mg of the title compound as a white powder. This powder was dissolved in the minimum volume of hot dimethyl sulfoxide and boiling water was added. Colourless plates of (I) formed on cooling and leaving overnight, and were collected after the solvents were decanted.

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Crystal data

$C_{21}H_{16}N_2O$
$M_r = 312.36$
Orthorhombic, $P2_12_12$
$a = 11.284$ (3) Å
$b = 14.918$ (4) Å
$c = 4.5942$ (11) Å
$V = 773.4$ (3) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 93$ (2) K
0.20 × 0.10 × 0.01 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2004)
$T_{\min} = 0.983$, $T_{\max} = 0.999$
5088 measured reflections
869 independent reflections
761 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.150$
$S = 1.14$
869 reflections
114 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
N1—H1···O1$^{\rm i}$	0.85 (4)	2.06 (4)	2.856 (4)	157 (4)

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

The N-bound H atom was located in a difference map and its position was freely refined, with $U_{\rm iso}(\mathrm{H}) = 1.2U_{\rm eq}(\mathrm{N})$. The C-bound H atoms were positioned geometrically, with C—H = 0.95 Å, and refined as riding, with $U_{\rm iso}(\mathrm{H}) = 1.2U_{\rm eq}(\mathrm{C})$.

Data collection: *CrystalClear* (Rigaku, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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