

# Comparison of *N*-(3,4,5-trimethoxybenzylidene)naphthalen-1-amine and its reduction product *N*-(3,4,5-trimethoxybenzyl)naphthalen-1-amine

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Received 7 November 2013

Accepted 30 December 2013

The molecules in (*E*)-*N*-(3,4,5-trimethoxybenzylidene)naphthalen-1-amine, C<sub>20</sub>H<sub>19</sub>NO<sub>3</sub>, (I), and its reduction product *N*-(3,4,5-trimethoxybenzyl)naphthalen-1-amine, C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>, (II), are both conformationally chiral, but (I) crystallizes in a centrosymmetric space group, while (II) crystallizes with just one conformational enantiomer in each crystal. A combination of two C—H···O hydrogen bonds links the molecules of (I) into sheets containing a single type of R<sub>6</sub><sup>6</sup>(44) ring, and these sheets are linked into a continuous three-dimensional array by a single  $\pi$ – $\pi$  stacking interaction. The molecules of (II) are linked into complex sheets by a combination of N—H···O, C—H···O and C—H··· $\pi$ (arene) hydrogen bonds.

**Keywords:** crystal structure; supramolecular structure; hydrogen bonding.

## 1. Introduction

We report here the molecular and supramolecular structures of (*E*)-*N*-(3,4,5-trimethoxybenzylidene)naphthalen-1-amine, (I) (Fig. 1), and its reduction product *N*-(3,4,5-trimethoxybenzyl)naphthalen-1-amine, (II) (Fig. 2). Compound (I) was prepared using a thermal condensation reaction between 1-naphthylamine and 3,4,5-trimethoxybenzaldehyde, and (II) was prepared from (I) by reduction with sodium borohydride.

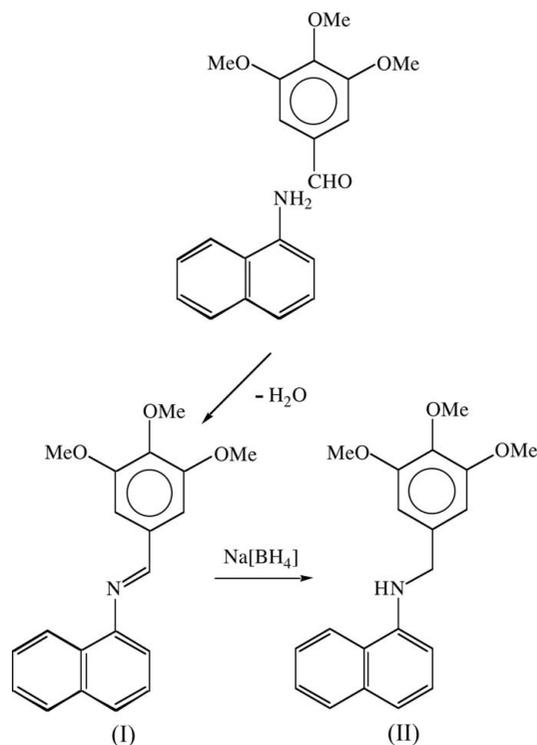
## 2. Experimental

### 2.1. Synthesis and crystallization

For the synthesis of (I), a mixture of 1-naphthylamine (2.1 mmol) and 3,4,5-trimethoxybenzaldehyde (2.1 mmol) was heated in an oil bath at 423 K for 8 min until complete disappearance of the starting materials, as monitored by thin-

layer chromatography (TLC). The mixture was cooled to ambient temperature and the resulting brown solid was triturated with ethanol to afford the title compound, (I), as brown crystals (yield 86%; m.p. 402 K). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3015, 2991, 2953, 2932, 2831, 1618 (C=N), 1578 (C=C), 1502, 1331, 1227 (C—O), 1130 (C—O), 772.

For the synthesis of (II), a twofold molar excess of sodium borohydride was added in portions over a period of 15 min to a solution of (I) (0.400 g) in ethanol (12 ml). After complete disappearance of the starting compound, (I), as monitored by TLC, the solvent was removed under reduced pressure, an excess of water was added and the product was exhaustively extracted with ethyl acetate. The combined organic extracts were dried using anhydrous sodium sulfate. The drying agent was then removed by filtration and the solvent removed under reduced pressure to afford (II) as pale-yellow crystals (yield 98%; m.p. 412 K). FT-IR (KBr,  $\nu$ , cm<sup>-1</sup>): 3413 (N—H), 3004, 2933, 2836, 1586 (C=C), 1532, 1504, 1237 (C—O), 1114 (C—O), 1005, 778.



Crystals of (I) and (II) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in air, of the corresponding solutions in methanol.

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and were then treated as riding. C-bound H atoms were permitted to ride in geometrically idealized positions, with C—H = 0.95 (aromatic and alkenyl), 0.98 (CH<sub>3</sub>) or 0.99 Å (CH<sub>2</sub>) and  $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$ , where  $k = 1.5$  for the methyl groups, which were permitted to rotate but not to tilt,

Table 1

Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C <sub>20</sub> H <sub>19</sub> NO <sub>3</sub>	C <sub>20</sub> H <sub>21</sub> NO <sub>3</sub>
<i>M<sub>r</sub></i>	321.36	323.38
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	120	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.9697 (11), 9.3300 (9), 19.9254 (12)	9.4460 (17), 11.0868 (18), 15.8195 (16)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 93.846 (8), 90	90, 90, 90
<i>V</i> (Å <sup>3</sup> )	1663.8 (3)	1656.7 (4)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.09	0.09
Crystal size (mm)	0.29 × 0.28 × 0.20	0.41 × 0.39 × 0.32
Data collection		
Diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.958, 0.983	0.955, 0.973
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	23021, 3820, 2117	16040, 2168, 1799
<i>R<sub>int</sub></i>	0.070	0.078
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.650	0.650
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.060, 0.170, 1.02	0.042, 0.105, 1.09
No. of reflections	3820	2168
No. of parameters	220	220
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.29, -0.28	0.21, -0.18

Computer programs: *COLLECT* (Nonius, 1999), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SIR2004* (Burla *et al.*, 2005), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

and *k* = 1.2 for all other C-bound H atoms. The H atom bonded to atom N1 in (II) was permitted to ride at the position located in a difference map, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N), giving an N–H distance of 0.97 Å. Several low-angle reflections, *viz.* (101) in (I) and (101) and (002) in (II), which had been wholly or partially attenuated by the beam-stop, were omitted from the data sets. In the absence of significant resonant scattering, the Flack *x* parameter (Flack, 1983) for (II) was indeterminate (Flack & Bernardinelli, 2000); accordingly, the Friedel-equivalent reflections for (II) were merged prior to the final refinements. It was not possible, therefore, to determine the absolute configuration of the molecule in the crystal of (II) selected for data collection. The reference molecule for (II) was selected to have the same sign for the C13–C14–O14–C24 torsion angle as that in the reference molecule for (I).

### 3. Results and discussion

Despite their similar molecular constitutions, (I) and (II) crystallize in very different space groups, *viz.* the centrosymmetric monoclinic space group *P*2<sub>1</sub>/*n* in the case of (I) and the Sohnke orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> in the case of (II). Both compounds crystallize with *Z* = 4 in unit cells of very similar volume, although it is perhaps surprising that the unit-cell volume for (I) is marginally greater than that for (II), presumably reflecting the stronger intermolecular hydrogen-bonding in (II) (see below). Consistent with this, the density of (II) (1.296 Mg m<sup>-3</sup>) is slightly greater than that of (I) (1.283 Mg m<sup>-3</sup>).

In neither compound are the ring systems exactly coplanar with the central C–N–C–C linking unit, as indicated by the leading torsion angles (Tables 2 and 3). The torsion angle defining the orientation of the trimethoxyphenyl ring with

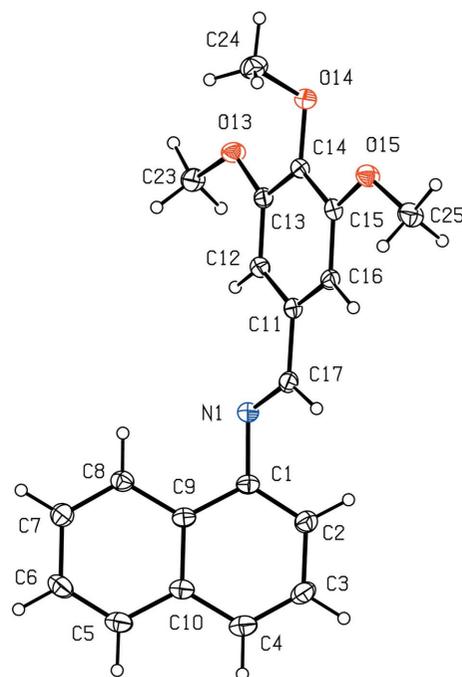


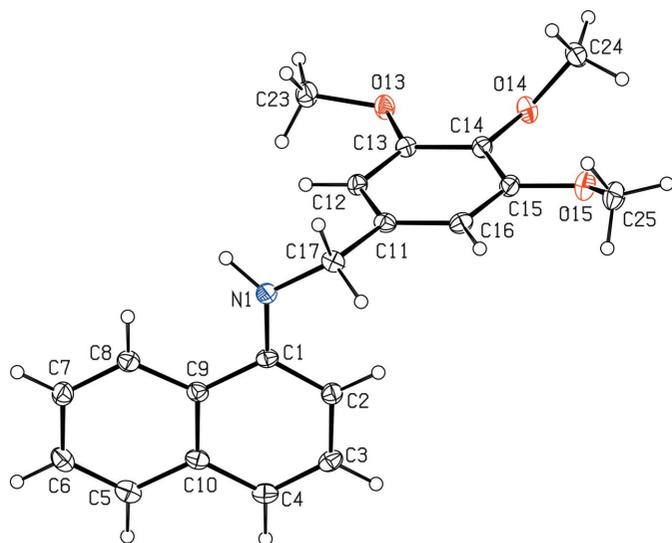
Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

**Table 2**  
Selected geometric parameters (Å, °) for (I).

N1—C17	1.280 (2)		
C1—N1—C17	117.48 (18)	O14—C14—C13	119.71 (19)
N1—C17—C11	122.34 (19)	O14—C14—C15	120.35 (18)
O13—C13—C12	125.09 (19)	O15—C15—C14	115.33 (19)
O13—C13—C14	114.47 (19)	O15—C15—C16	124.92 (19)
C2—C1—N1—C17	−46.8 (3)	C12—C13—O13—C23	2.8 (3)
C1—N1—C17—C11	179.99 (19)	C13—C14—O14—C24	90.8 (2)
N1—C17—C11—C12	−8.7 (3)	C16—C15—O15—C25	8.6 (3)

respect to the central spacer unit in compound (I) is close to zero, but there is no metrical evidence for any electronic delocalization across the spacer unit. The dihedral angle between the trisubstituted aryl ring and the naphthalene system in (I) is 55.4 (2)°, whereas in (II) this angle is 88.2 (2)°. In both compounds, atom C24 of the 4-methoxy substituent is considerably displaced from the plane of the adjacent aryl ring, by 1.224 (3) Å in (I) and 1.018 (3) Å in (II). A conformation having atom C24 nearly coplanar with the adjacent aryl ring is precluded by the steric congestion between atom C24 and atoms O13 or O15 which would thereby result. Similar conformations have been observed in other 3,4,5-trimethoxyphenyl derivatives (Trilleras *et al.*, 2005; Peralta *et al.*, 2007; Cuervo *et al.*, 2009). For compound (II), the torsion angles (Table 3) indicate considerable deviation from planarity for atoms C23 and C25 of the 3-methoxy and 5-methoxy substituents, which are displaced from the plane of the adjacent ring by 0.252 (3) and 0.468 (3) Å, respectively, as opposed to displacements of only 0.043 (3) and 0.128 (3) Å, respectively, in (I). However, in both compounds, the two C—C—O angles at atom C14 have fairly similar values, whereas the corresponding pairs of values at atoms C13 and C15 differ by *ca* 10° (Tables 2 and 3), as typically found (Seip & Seip, 1973; Ferguson *et al.*, 1996) for methoxyaryl systems in which



**Figure 2**  
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

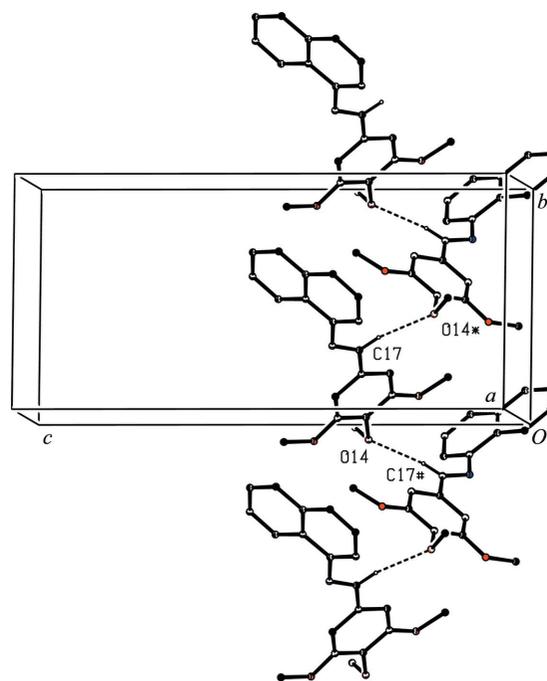
**Table 3**  
Selected geometric parameters (Å, °) for (II).

N1—C17	1.443 (3)		
C1—N1—C17	122.3 (2)	O14—C14—C13	117.6 (2)
N1—C17—C11	116.8 (2)	O14—C14—C15	122.8 (2)
O13—C13—C12	124.2 (2)	O15—C15—C14	116.2 (2)
O13—C13—C14	115.0 (2)	O15—C15—C16	123.9 (2)
C2—C1—N1—C17	−5.3 (4)	C12—C13—O13—C23	10.2 (3)
C1—N1—C17—C11	73.6 (3)	C13—C14—O14—C24	126.2 (2)
N1—C17—C11—C12	33.4 (3)	C16—C15—O15—C25	−26.3 (4)

the methoxy C atom is effectively coplanar with the adjacent aryl ring. The N1—C17 distances are clearly consistent with the different oxidation levels in (I) and (II), and it is interesting to note the relative values of the bond angles at atoms N1 and C17, but no simple rationalization for this is possible.

The molecules of (I) and (II) exhibit no internal symmetry and hence they are both conformationally chiral. No evidence for twinning was found for compound (II) and, in the absence of inversion or reflection twinning, each crystal can contain only one conformational enantiomer. There is no reason to suppose that one conformational enantiomer is preferred over the other, and hence it seems likely that compound (II) crystallizes as a conformational conglomerate, while compound (I) crystallizes as a conformational racemate.

The molecules of (I) are linked into a three-dimensional array in the form of  $\pi$ -stacked hydrogen-bonded sheets. The sheets are built using two C—H...O hydrogen bonds (Table 4)



**Figure 3**  
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded C(7) chain parallel to [010]. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*) or a hash symbol (#) are at the symmetry positions  $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$  and  $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ , respectively.

**Table 4**

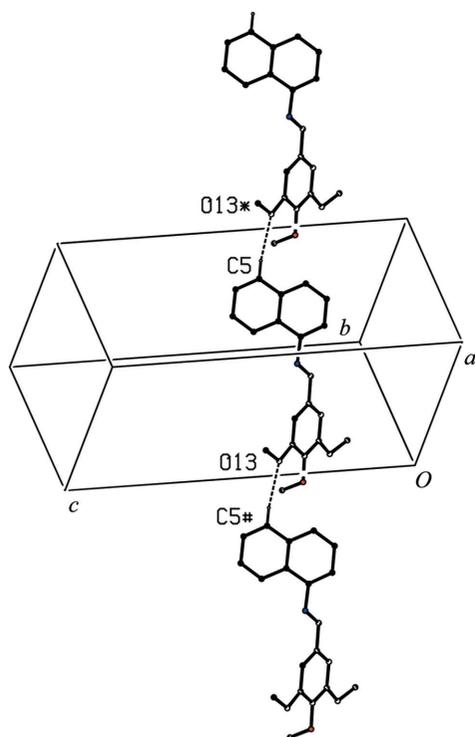
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5-H5\cdots O13^i$	0.95	2.52	3.454 (3)	169
$C17-H17\cdots O14^{ii}$	0.95	2.40	3.331 (2)	166

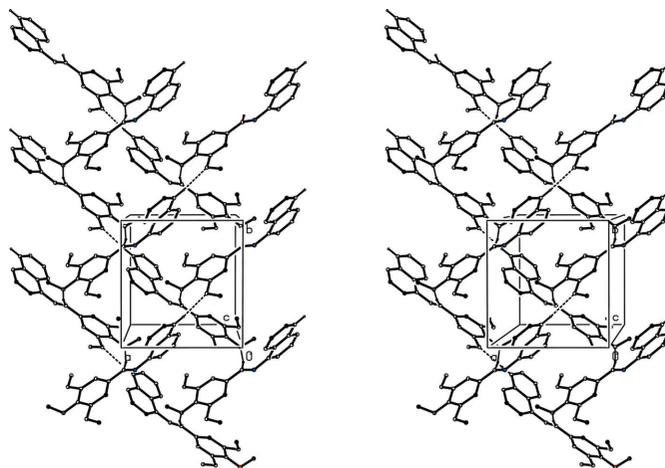
Symmetry codes: (i)  $x + 1, y + 1, z$ ; (ii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ .

and their formation is readily analysed in terms of two one-dimensional substructures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). Molecules related by the  $2_1$  screw axis along  $(\frac{1}{4}, y, \frac{1}{4})$  are linked by the shorter hydrogen bond to form a  $C(7)$  chain (Bernstein *et al.*, 1995) running parallel to the [010] direction (Fig. 3). In addition, molecules related by translation are linked by the longer of the two hydrogen bonds to form a  $C(11)$  chain running parallel to the [110] direction (Fig. 4). The combination of chains along [010] and [110] generates a sheet lying parallel to (001) and built from a single type of  $R_6^6(44)$  ring (Fig. 5).

Two sheets of this type, related to one another by inversion, pass through each unit cell, in the domains  $0 < z < \frac{1}{2}$  and  $\frac{1}{2} < z < 1.0$ , respectively, and all of the sheets are linked into a three-dimensional structure by the action of a single aromatic  $\pi$ - $\pi$  stacking interaction. The C5–C10 rings in the molecules at  $(x, y, z)$  and  $(-x + 2, -y + 1, -z + 1)$ , which lie in different hydrogen-bonded sheets, are strictly parallel, with an interplanar spacing of 3.480 (2) Å; the ring-centroid separation is

**Figure 4**

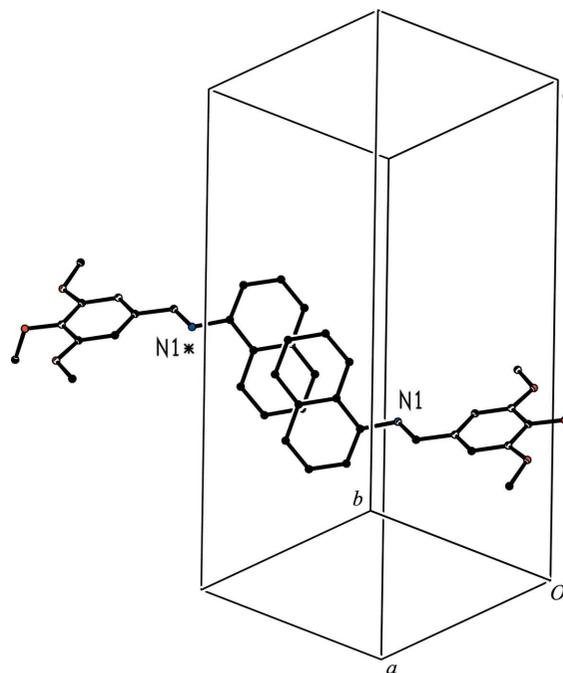
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded  $C(11)$  chain parallel to [110]. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*) or a hash symbol (#) are at the symmetry positions  $(x + 1, y + 1, z)$  and  $(x - 1, y - 1, z)$ , respectively.

**Figure 5**

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet of  $R_6^6(44)$  rings parallel to (001). Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

3.798 (2) Å, corresponding to a near-ideal ring-centroid offset of 1.521 (2) Å (Fig. 6). Propagation of this interaction by the space-group symmetry operators is sufficient to link all of the hydrogen-bonded sheets.

There are four independent hydrogen bonds in the crystal structure of (II) (Table 5), including an  $N-H\cdots O$  hydrogen bond, which is necessarily absent from the structure of (I). However, despite the large number of hydrogen bonds in (II), the supramolecular assembly is only two-dimensional. The overall sheet structure is of considerable complexity but, as in

**Figure 6**

Part of the crystal structure of (I), showing the formation of the  $\pi$ - $\pi$  stacking interaction which links adjacent hydrogen-bonded sheets. For the sake of clarity, all H atoms have been omitted. The atom marked with an asterisk (\*) is at the symmetry position  $(-x + 2, -y + 1, -z + 1)$ .

**Table 5**

Hydrogen-bond geometry (Å, °) for (II).

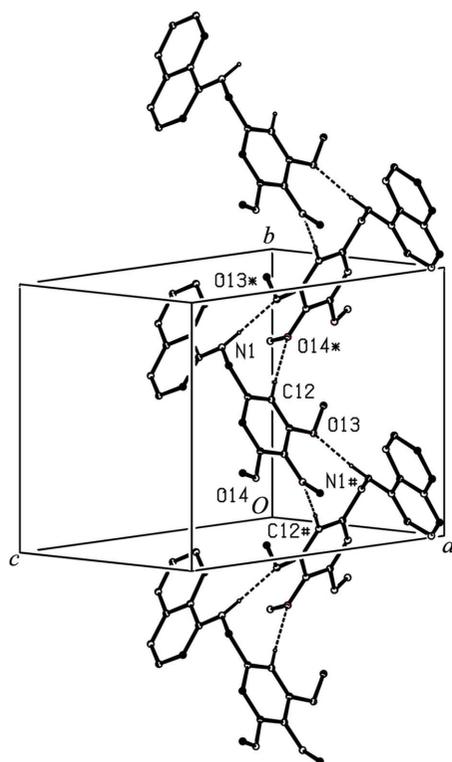
Cg1 represents the centroid of the C11–C16 ring and Cg2 represents the centroid of the C1–C4/C10/C9 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 $\cdots$ O13 <sup>i</sup>	0.97	2.07	3.016 (3)	163
C12–H12 $\cdots$ O14 <sup>i</sup>	0.95	2.59	3.535 (3)	176
C4–H4 $\cdots$ Cg1 <sup>ii</sup>	0.95	2.69	3.632 (3)	173
C7–H7 $\cdots$ Cg2 <sup>iii</sup>	0.95	2.86	3.677 (3)	145

Symmetry codes: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x, y + \frac{1}{2}, -z + \frac{1}{2}$ .

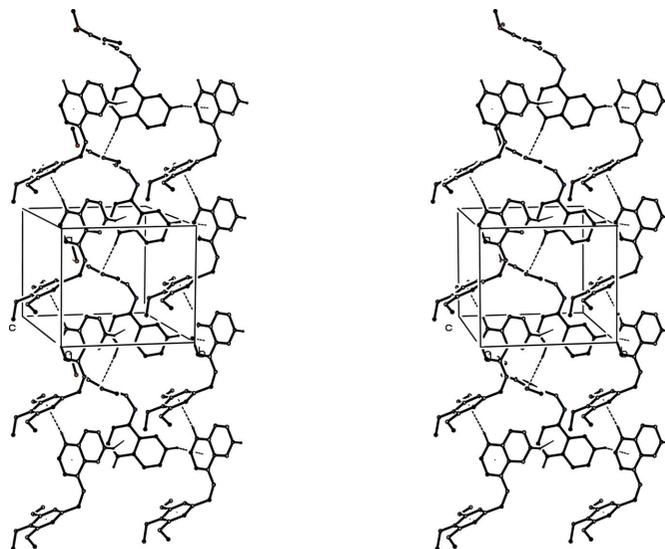
(I), its formation can be analysed in terms of simple substructures. The N–H $\cdots$ O hydrogen bond links molecules related by the  $2_1$  screw axis along  $(\frac{1}{2}, y, \frac{1}{4})$  into a  $C(7)$  chain running parallel to the [010] direction, and this chain formation is enhanced by a rather long, but nearly linear, C–H $\cdots$ O hydrogen bond which forms a  $C(5)$  motif, so that these two interactions together generate a  $C(5)C(7)[R_2^2(10)]$  chain of rings (Fig. 7).

This chain of rings actually lies within a sheet generated by the two C–H $\cdots\pi$ (arene) hydrogen bonds. The interaction having atom C4 as the donor links molecules related by translation into a chain running parallel to the [100] direction, while that involving atom C7 as the donor links molecules related by the  $2_1$  screw axis along  $(0, y, \frac{1}{4})$  into a chain running



**Figure 7**

Part of the crystal structure of (II), showing the formation of a hydrogen-bonded  $C(5)C(7)[R_2^2(10)]$  chain of rings parallel to [010]. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*) or a hash symbol (#) are at the symmetry positions  $(-x + 1, y + \frac{1}{2}, -z + \frac{1}{2})$  and  $(-x + 1, y - \frac{1}{2}, -z + \frac{1}{2})$ , respectively.



**Figure 8**

A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded sheet parallel to (001). Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

parallel to the [010] direction. In combination, these two chains generate a sheet lying parallel to (001) (Fig. 8). Two sheets pass through each unit cell, in the domains  $0 < z < \frac{1}{2}$  and  $\frac{1}{2} < z < 1.0$ , and containing screw axes at  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$ , respectively. The only possible direction-specific interaction between molecules in adjacent sheets is a C–H $\cdots\pi$ (arene) contact, which not only involves a C–H bond of low acidity but is characterized by a rather long H $\cdots$ A distance, 2.94 Å, so that this contact is unlikely to be structurally significant.

The authors thank the Centro de Instrumentación Científico-Técnica of the Universidad de Jaén and the staff for the data collection. AG and RA thank COLCIENCIAS and the Universidad del Valle for financial support. JC thanks the Consejería de Innovación, Ciencia y Empresa (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support.

Supporting information for this paper is available from the IUCr electronic archives (Reference: SF3215).

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