

## 2-Oxo-2-phenyl-*N*-[(*R*)-1-phenylethyl]acetamide and *N,N*-dimethyl-2-(1-naphthyl)-2-oxoacetamide: possibility of Yang photocyclization in a crystal

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Received 17 June 2009

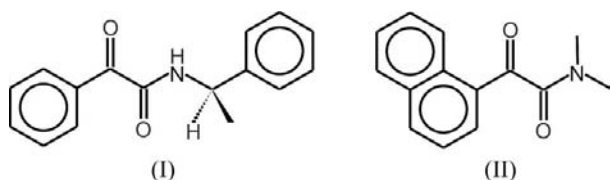
Accepted 1 July 2009

Online 9 July 2009

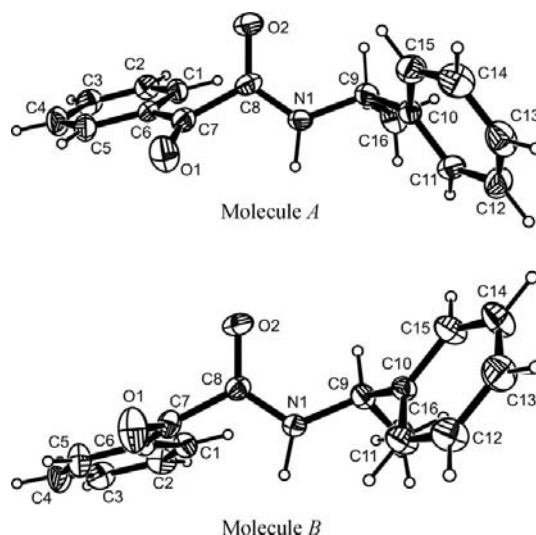
The crystal structures of 2-oxo-2-phenyl-*N*-[(*R*)-1-phenylethyl]acetamide,  $C_{16}H_{15}NO_2$ , (I), and *N,N*-dimethyl-2-(1-naphthyl)-2-oxoacetamide,  $C_{14}H_{13}NO_2$ , (II), were determined in an attempt to understand the reason for the lack of Yang photocyclization in their respective crystals. In the case of (I), the long distance between the O atom of the carbonyl group and the  $\gamma$ -H atom, and between the C atom of the carbonyl group and the  $\gamma$ -C atom, preclude Yang photocyclization. For (II), the deviation of the  $\gamma$ -H atom from the plane of the carbonyl group and interactions between the naphthalene rings are regarded as possible reasons for the chemical inertia. The two independent molecules of (I) differ in their conformation.  $N-H\cdots O$  hydrogen bonds link molecules of (I) into chains extended along the *b* axis.

### Comment

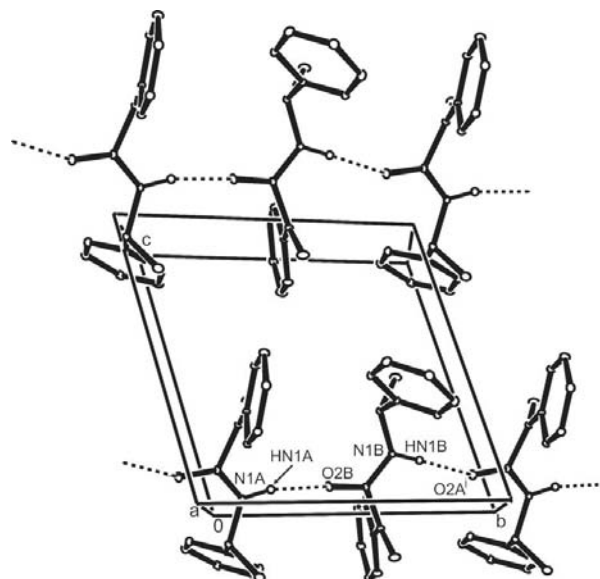
Structural changes in crystals due to photochemical reactions are the main subject of our studies. In particular, we examine geometric changes at the reaction centre and the movement of molecules and their fragments in crystals. Studies of this type enable us to determine and understand the pathway of chemical reactions in the crystalline state and to gain knowledge of the differences and similarities that are characteristic for a given type of reaction proceeding in different compounds.



Studies of this type concern intermolecular (Fernandes & Levendis, 2004; Ohba & Ito, 2003; Turowska-Tyrk, 2001, 2003;



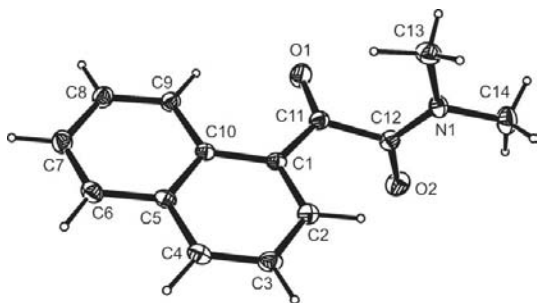
**Figure 1**  
Views of molecules *A* and *B* of (I), showing the atom-numbering schemes (suffixes *A* and *B* have been omitted from the atom labels). Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.



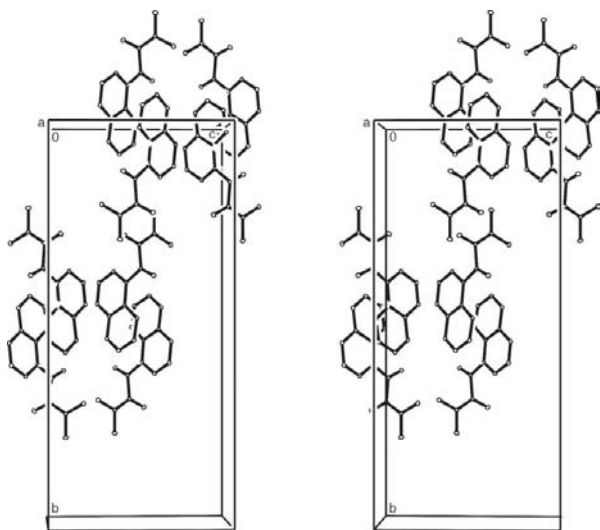
**Figure 2**  
The hydrogen bonding (dashed lines) in the structure of (I), viewed approximately along the *a* axis. Only H atoms taking part in hydrogen bonds are shown. [Symmetry code: (i)  $x, 1 + y, z$ .]

Turowska-Tyrk & Trzop, 2003) and intramolecular photochemical reactions (Cotton *et al.*, 2007; Turowska-Tyrk, Bąkiewicz, Scheffer & Xia, 2006; Turowska-Tyrk, Trzop, Scheffer & Chen, 2006; Turowska-Tyrk, Bąkiewicz & Scheffer, 2007; Turowska-Tyrk, Łabęcka, Scheffer & Xia, 2007; Trzop & Turowska-Tyrk, 2008; Zheng *et al.*, 2007). In this paper, we present the structures of the two title compounds, 2-oxo-2-phenyl-*N*-[(*R*)-1-phenylethyl]acetamide, (I), and *N,N*-dimethyl-2-(1-naphthyl)-2-oxoacetamide, (II), which can potentially undergo an intramolecular Yang photocyclization.

Compound (I) crystallizes in the triclinic space group *P*1, with two crystallographically independent molecules in the



**Figure 3**  
A view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.



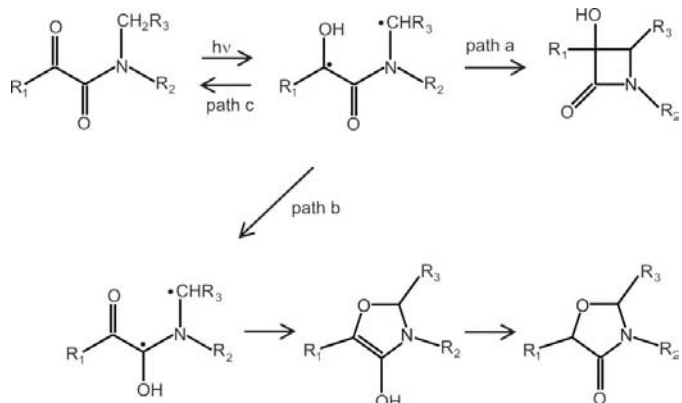
**Figure 4**  
A stereoscopic view of the crystal lattice fragment of (II), illustrating the  $\pi$ - $\pi$  stacking of the naphthyl groups.

asymmetric unit. Fig. 1 presents projections of molecules *A* and *B* on the  $C7A/C8A/O2A/N1A$  and  $C7B/C8B/O2B/N1B$  planes, respectively, clearly showing the conformational differences. The largest differences are seen for the torsion angles  $N1-C9-C10-C11$  and  $C16-C9-C10-C11$ , which are  $96.2(6)$  and  $-28.3(7)^\circ$ , respectively, for molecule *A*, and  $37.6(7)$  and  $-85.9(6)^\circ$ , respectively, for molecule *B*. Hydrogen bonds of the type  $N-H \cdots O$  link molecules *A* and *B* into extended chains in the *b*-axis direction (Fig. 2 and Table 1).

Compound (II) crystallizes in the orthorhombic space group *Pbca* with only one molecule in the asymmetric unit (Fig. 3). In contrast with compound (I), there are no classical hydrogen bonds. The naphthalene rings are arranged in parallel pairs, with a perpendicular distance between the rings of  $3.506(1)$  Å and a centroid-centroid distance of  $3.683$  Å (Fig. 4).

Compounds (I) and (II) have a characteristic molecular fragment, namely the carbonyl group and a  $\gamma$ -H atom. Compounds with such a structure can potentially undergo an intramolecular Norrish type II photochemical reaction. A

mechanism for this reaction is presented in the reaction scheme (Aoyama *et al.*, 1979; Lavy *et al.*, 2008; Yang *et al.*, 2005). The first step is a  $\gamma$ -H abstraction by the carbonyl O atom and the formation of a biradical which can then undergo three reaction types: (i) a Yang photocyclization leading to the formation of a cyclobutane ring (path 'a'), (ii) a 1,4-hydrogen shift leading to the formation of a five-membered ring (path 'b') or (iii) a return to the initial reactant (path 'c').



Several geometric demands must be fulfilled in order that Yang photocyclization can proceed (Natarajan *et al.*, 2005; Xia *et al.*, 2005). They concern the following parameters: the  $(C)O \cdots \gamma\text{-H}$  distance  $d$ , the  $(O)C \cdots \gamma C$  distance  $D$ , the deviation  $\omega$  of  $\gamma\text{-H}$  from the mean plane of the carbonyl group, the  $C=O \cdots \gamma\text{-H}$  angle  $\Delta$  and the  $\gamma\text{-C}-\gamma\text{-H} \cdots O$  angle  $\Theta$ . The ideal and average literature values for these parameters, together with the data for compound (II), are given in Table 2. For (I), the geometric demands are not fulfilled. The values of  $d$  and  $D$  are too large at  $3.72$  and  $3.46$  Å, respectively, which explains the chemical inertia of (I) in the crystalline state. It seems that (II) meets the geometric demands for Yang photocyclization, although the influence of the  $\omega$  parameter is not fully clear. Nevertheless, despite UV-Vis irradiation of a crystal with a 100 W Hg lamp (7 h), Yang photocyclization did not proceed. We did not observe any changes in the cell constants over the irradiation time and the structure determined after irradiation revealed only molecules of the reactant.

There can be several reasons for this inertia of compound (II). One of them was mentioned above, *viz.* the value of the  $\omega$  parameter is about  $13^\circ$  greater than the largest angle observed for compounds undergoing Yang photocyclization (Turowska-Tyrk, Bąkiewicz & Scheffer, 2007). Interactions between the naphthalene rings (Fig. 4) could be another cause. Such an explanation was proposed for 2,4,6-triisopropylbenzophenones (Ito *et al.*, 2009). The next reason for the chemical inertia of (II) can be related to the size of the reaction cavity. Such a reason was given in the case of inclusion compounds (Zouev *et al.*, 2006), styrylcoumarins (Moorthy *et al.*, 2006) and 2,4,6-triisopropylbenzophenones (Ito *et al.*, 1998). Interactions between naphthalene rings, as well as a small reaction cavity, restrain the molecular movements necessary for the chemical reaction to proceed. In order to make molecular movements easier, the crystal of (II) was irradiated at a higher tempera-

ture (323 K), but this did not help to induce a reaction. It is also possible that the photochemical reaction did not proceed owing to the absorption of UV–Vis radiation by a naphthalene group in a molecule (Natarajan *et al.*, 2005). The lack of a photochemical reaction in compound (II) cannot be a result of rotation of a methyl group because such rotation is not observed in the crystal.

## Experimental

Compounds (I) and (II) were purchased from Sigma–Aldrich and recrystallized from toluene.

### Compound (I)

#### Crystal data

$C_{16}H_{15}NO_2$	$\gamma = 113.75 (3)^\circ$
$M_r = 253.29$	$V = 676.6 (3) \text{ \AA}^3$
Triclinic, $P1$	$Z = 2$
$a = 8.593 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.761 (2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 10.054 (3) \text{ \AA}$	$T = 299 \text{ K}$
$\alpha = 93.32 (2)^\circ$	$0.50 \times 0.30 \times 0.15 \text{ mm}$
$\beta = 114.45 (3)^\circ$	

#### Data collection

Kuma KM-4-CCD diffractometer	1671 reflections with $I > 2\sigma(I)$
3656 measured reflections	$R_{\text{int}} = 0.043$
2248 independent reflections	

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$	H atoms treated by a mixture of
$wR(F^2) = 0.170$	independent and constrained
$S = 1.05$	refinement
2248 reflections	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
349 parameters	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
3 restraints	

### Compound (II)

#### Crystal data

$C_{14}H_{13}NO_2$	$V = 2353.8 (13) \text{ \AA}^3$
$M_r = 227.25$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 8.981 (3) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 24.056 (8) \text{ \AA}$	$T = 299 \text{ K}$
$c = 10.895 (3) \text{ \AA}$	$0.50 \times 0.20 \times 0.05 \text{ mm}$

#### Data collection

Kuma KM-4-CCD diffractometer	1229 reflections with $I > 2\sigma(I)$
11922 measured reflections	$R_{\text{int}} = 0.051$
2058 independent reflections	

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$	H atoms treated by a mixture of
$wR(F^2) = 0.158$	independent and constrained
$S = 1.11$	refinement
2058 reflections	$\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$
196 parameters	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$

H atoms for (I) were positioned geometrically and treated as riding, with C–H = 0.93–0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for a methyl H atoms or  $1.2U_{\text{eq}}(\text{C})$  for other H atoms. The N-bound H atom in (I)

**Table 1**

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1A-HN1A\cdots O2B$	0.97 (6)	1.92 (6)	2.864 (5)	166 (5)
$N1B-HN1B\cdots O2A^i$	0.98 (6)	1.91 (6)	2.889 (5)	178 (5)

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

**Table 2**

Values of the geometric parameters (Å, °) characteristic of a Yang photocyclization.

	$d$	$D$	$\omega$	$\Delta$	$\Theta$
Ideal value	<2.7		0	90–120	180
Average literature value†	2.64 (8)	3.00 (9)	54 (10)	82 (8)	116 (3)
Range‡	2.49–2.82	2.82–3.12	49.0–67.5	52.9–88.0	111.0–128.0
Average literature value§	2.71±0.08		52.9±1.7	57.2±3.3	119.6±4.95
(II) (this work)	2.72 (4)	2.857 (5)	80.4 (10)	58.4 (8)	112.4 (13)

† These mean values of  $d$ ,  $\omega$  and  $\Delta$  are given for 57 and  $\Theta$  for 40 aromatic ketones undergoing a Yang photocyclization (Natarajan *et al.*, 2005), and  $D$  for 53 structures (Xia *et al.*, 2005). ‡ The ranges of the parameters are given on the basis of 47 compounds for  $d$ ,  $\omega$ ,  $\Delta$  and  $\Theta$  (Turowska-Tyrk, Bąkiewicz & Scheffer, 2007; Turowska-Tyrk, Łabęcka, Scheffer & Xia, 2007; Turowska-Tyrk & Trzop, 2003; Natarajan *et al.*, 2005; Chen *et al.*, 2005; Ihmels & Scheffer, 1999; Leibovitch *et al.*, 1998; Vishnumurthy *et al.*, 2002) and 15 compounds for  $D$  (Turowska-Tyrk, Bąkiewicz & Scheffer, 2007; Turowska-Tyrk, Łabęcka, Scheffer & Xia, 2007; Turowska-Tyrk & Trzop, 2003; Leibovitch *et al.*, 1998). § The average values of  $d$ ,  $\omega$ ,  $\Delta$  and  $\Theta$  are based on nine examples of  $\alpha$ -oxoamides undergoing  $\gamma$ -H abstraction (Natarajan *et al.*, 2005).

was located in a difference Fourier map and refined without constraints. For (II), the H atoms on atom C14 were located in a difference Fourier map and refined as part of a rigid rotating group. The remaining H atoms were found in a difference Fourier map and refined without constraints.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3330). Services for accessing these data are described at the back of the journal.

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