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(R,R)-(−)-*trans*-1,4-Dioxaspiro[4,5]decane-2,3-diylbis(diphenylmethanol) *N*-allyl-*N*-propyl-3-oxo-1-cyclohexenecarboxamide (2/1 inclusion compound)

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In the title inclusion compound, $2C_{34}H_{34}O_4\cdot C_{13}H_{19}NO_2$, the *N*-allyl moiety is located closer to the cyclohexenone ring than the *N*-propyl group in the guest amide. In the crystal structure, two keto O atoms of the guest molecule act as acceptors of O—H···O hydrogen bonds with the two host molecules.

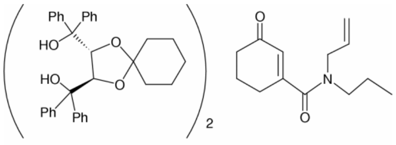
Key indicators

Single-crystal X-ray study
T = 248 K
Mean σ(C–C) = 0.009 Å
R factor = 0.062
wR factor = 0.172
Data-to-parameter ratio = 7.0

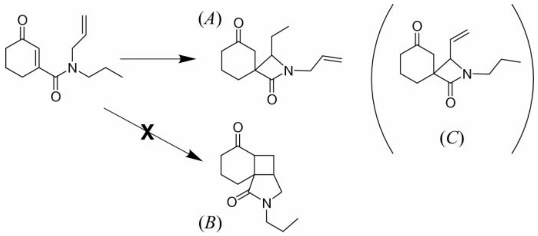
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Organic solid-state photoreactions of guest molecules in inclusion compounds with chiral hosts are efficient methods to achieve regioselective and enantioselective syntheses (Tanaka *et al.*, 1992; Toda *et al.*, 1993). The enantioselective intramolecular photocyclization reaction of *N*-allyl-*N*-*R*-3-oxo-1-cyclohexenecarboxamides (R = Me, Et, ^{n}Pr *etc.*) in inclusion crystals was reported by Toda *et al.* (1995). The products obtained were tricyclic compounds, as the result of a [2 + 2]-photoreaction in the guest molecule, except for that with R = ^{n}Pr, which gave the spiro β-lactam (A), not the tricyclic compound (B). The crystal structure of the title compound, (I), has been determined to investigate the conformation of the guest amide (R = ^{n}Pr).



(I)



The n-propyl atoms C23 and C24 of the guest molecule show large elongated displacement ellipsoids, suggesting some positional disorder (Fig. 1). On the other hand, the *N*-allyl group C19/C20/C21 has normal displacement parameters and normal geometry (Table 1). The center-to-center distance between the C16=C17 and C20=C21 double bonds is 4.23 (1) Å, and they are inclined to one another by an angle of 95.0 (7)°. This arrangement is not suitable for [2+2]-photocyclization, and will give product (C) not (A). Therefore, the structure determined in the present study is not consistent with the photoreactivity reported by Toda *et al.* (1995). One of the possibilities, which could cause this inconsistency, is a relatively rare polymorphism of these inclusion compounds

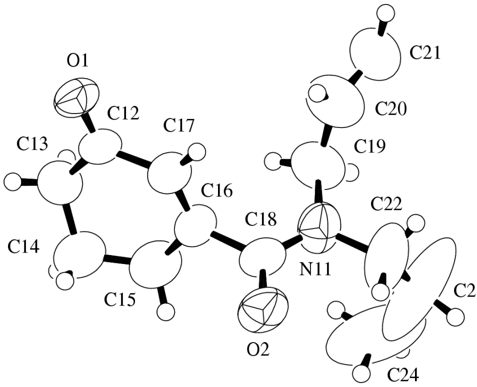


Figure 1
The structure of the guest molecule, with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

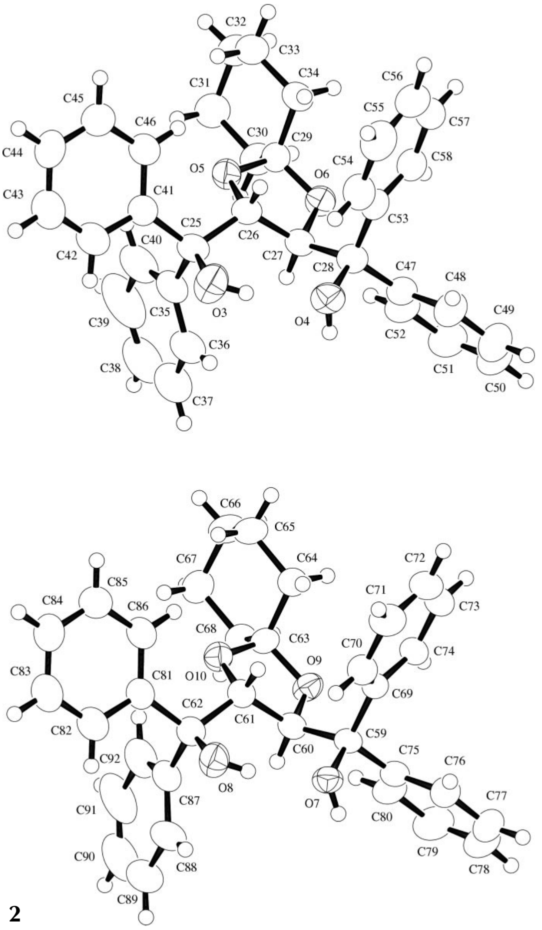


Figure 2
The structures of the two independent host molecules, with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

(Ohba *et al.*, 2000). The host molecule of (I) itself shows polymorphism; orthorhombic (Toda *et al.*, 1997; Nishikawa *et al.*, 1998) and triclinic (Hamazaki *et al.*, 1999) forms are known.

There are two independent host molecules in (I), which have similar conformations (Fig. 2). There is an intramolecular O—H···O hydrogen bond in both host molecules (Table 2). The guest molecule is also connected to the two host molecules by O—H···O hydrogen bonds (Table 2 and Fig. 3).

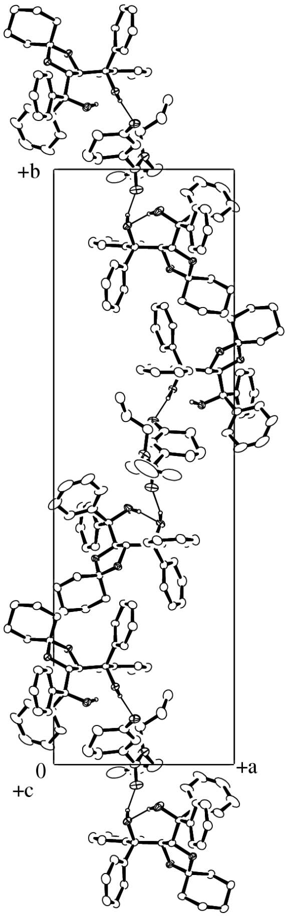


Figure 3
The projection of the crystal structure of (I), viewed along *c*, with thin lines indicating hydrogen bonding.

For a six-membered ring host, as in (I), and a corresponding five-membered ring host, which differ only in the size of the cycloalkane ring, it has been found that the crystal structures of their clathrate compounds are usually different (Ohba *et al.*, 2000). However, the crystal structure of an inclusion compound (II) of the same guest amide ($R = {}^{n}$Pr), with the corresponding five-membered ring host, was not determined in the present study. There were too many parameters, the number of independent host and guest molecules being four and two, respectively. The crystals of (II), grown from a diethyl ether solution, are colourless prisms; $2C_{33}H_{32}O_4 \cdot C_{13}H_{19}NO_2$, triclinic, space group $P1$, $a = 34.738\ (4)$, $b = 9.5934\ (12)$, $c = 10.0715\ (19)$ Å, $\alpha = 90.278\ (12)$, $\beta = 93.993\ (11)$, $\gamma = 90.021\ (10)^\circ$, $V = 3348.2\ (8)$ Å^3, $Z = 2$ at 248 K. The crystal structure of the inclusion compound (III) of a guest amide (R = benzyl) with a five-membered ring host (host/guest = 2/1) has been reported by Akutsu *et al.* (1996). In (III), the *N*-allyl moiety is located close to the cyclohexenone ring, a suitable arrangement for [2 + 2]-photocyclization, as expected from the reactivity data (Toda *et al.*, 1995).

Experimental

The title inclusion compound, (I), was prepared by Toda *et al.* (1995). Suitable crystals of (I) were grown from a toluene solution.

Crystal data

$2C_{34}H_{34}O_4 \cdot C_{13}H_{19}NO_2$
M_r = 1234.58
Monoclinic, $P2_1$
a = 10.4041 (16) Å
b = 34.308 (4) Å
c = 9.5158 (12) Å
β = 93.338 (11)°
V = 3390.8 (8) Å^3
Z = 2

D_x = 1.209 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 25.3–27.4°
μ = 0.62 mm^{-1}
T = 248 K
Needle, colourless
0.80 × 0.20 × 0.05 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: by integration (Coppens *et al.*, 1965)
$T_{\min}$ = 0.831, $T_{\max}$ = 0.969
6683 measured reflections
5806 independent reflections
4617 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.081
$\theta_{\max}$ = 65°
$h = -5 \rightarrow 12$
$k = 0 \rightarrow 39$
$l = -11 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: 4.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.172
S = 1.02
5806 reflections
833 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.125P)^2 + 0.2381P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.218 (8)	C16—C17	1.344 (10)
O2—C18	1.216 (7)	C16—C18	1.490 (9)
N11—C18	1.328 (9)	C19—C20	1.48 (1)
N11—C19	1.507 (10)	C20—C21	1.33 (2)
C12—C17	1.47 (1)		
N11—C19—C20	113.7 (7)	C19—C20—C21	121.6 (9)
N11—C18—C16—C17	−82.8 (9)	C18—N11—C19—C20	103.9 (9)
N11—C19—C20—C21	138.6 (10)	C18—N11—C22—C23	108 (1)
N11—C22—C23—C24	−46 (2)	C25—C26—C27—C28	−96.4 (5)
C16—C18—N11—C19	−3.0 (10)	C59—C60—C61—C62	−94.6 (4)
C16—C18—N11—C22	−179.2 (8)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O4	0.82	1.87	2.683 (5)	169
O4—H4···O2	0.82	1.94	2.736 (6)	165
O7—H7···O1	0.82	2.01	2.825 (5)	173
O8—H8···O7	0.82	1.87	2.682 (4)	168

The reflections with $\theta > 60°$ could not be measured due to the blind region of the four-circle diffractometer, combined with a cooling apparatus. The hydroxyl H atoms were located from difference syntheses and allowed to ride on the O atoms with $U_{\rm iso}({\rm H}) = U_{\rm eq}({\rm O})$. The other H-atom positional parameters were calculated geometrically and fixed with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom). The absolute structure was assigned, based on the known absolute configuration of the host molecule derived from (+)-tartaric acid (Toda & Tanaka, 1988). The Flack (1983) parameter was −1.0 (5) before the Friedel pairs were averaged. The *n*-propyl atoms C23 and C24 of the guest molecule show large anisotropic displacement parameters, suggesting unresolved positional disorder.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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