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7-Benzoyl-2,3,4a,6-tetraphenyl-4a,5,6,7-tetrahydro-1*H*-[1,3]oxazino[3,2-*a*][1,5]-benzodiazepin-1-one

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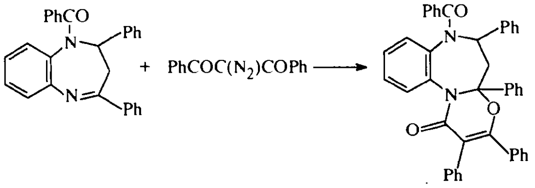
Abstract

The title compound, $C_{43}H_{32}N_2O_3$, has a *cis*-ring-fusion tricyclic structure which is formed from a benzene ring, a seven-membered diazepine ring and a 1,3-oxazinone ring. The 1,5-diazepine ring has a slightly distorted boat-like conformation, whereas the 1,3-oxazinone ring adopts a half-chair conformation.

Comment

Benzodiazepines are important pharmaceutical agents (Bunin *et al.*, 1994; Bock *et al.*, 1989). 4a,5,6,7-Tetrahydro-1*H*-[1,3]oxazino[3,2-*a*][1,5]benzodiazepin-1-ones (1,5-benzodiazepines fused with 1,3-oxazinone) with potential anxiolytic, anticonvulsant and antihypnotic activities (Sternbach, 1979), have been synthesized by Diels–Alder reactions of 2,4-diaryl-1-benzoyl-2,3-dihydro-1*H*-1,5-benzodiazepines and α-diazo-β-diketones (Capuano & Gartner, 1981; Capuano & Wamprecht, 1986). 2-Diazo-1,3-diphenyl-1,3-propanedione could take part in a thermal Wolff rearrangement to generate benzoyl phenylketene as the diene participating in the Diels–Alder reactions with 2,4-diaryl-1-benzoyl-2,3-dihydro-1*H*-1,5-benzodiazepines to obtain 4a,6-diaryl-1-benzoyl-2,3-diphenyl-4a,5,6,7-tetrahydro-1*H*-[1,3]oxazino[3,2-*a*][1,5]benzodiazepin-1-ones (Xu & Jin, 1994). Crystal structures of such compounds have not been reported. In order to elucidate the structures of the cycloadducts in these Diels–Alder reactions and to study their conformations, one of them, the title compound, (I), was subjected to X-ray diffraction analysis.



(I)

The molecular backbone of (I) is a tricyclic system formed by a benzene ring, a seven-membered diazepine ring and a 1,3-oxazinone ring. The central seven-membered ring is in a slightly distorted boat-like conformation, and is *cis*-fused to the 1,3-oxazinone ring at atoms N2 and C9, while the latter moiety is in a half-chair conformation. The phenyl group on C7 and the benzoyl group on N1 are both equatorial, and the phenyl group on C9 is axial to the central ring (Fig. 1), *i.e.* the cycloaddition reaction is a *cis*-addition reaction.

The interesting feature of the molecule is that the central ring adopts a slightly twisted boat-like conformation which is energetically not so favourable; this conformation is probably stabilized by the presence of the heteroatoms, especially the N atom with a large benzoyl group attached, and by the influence of the exocyclic bulky phenyl substituents attached to atoms C7 and C9.

The molecule contains two chiral C atoms, C7 and C9. The compound has a *rel*-(*R*–*S*) configuration. As a whole, the molecule possesses only C_1 symmetry because of the unsymmetrical nature of the substituents.

The two molecules in the asymmetric unit of the title compound are different because of packing effects, as can be deduced from their geometric parameters and the puckering parameters of their diazepine and oxazinone rings. The heterocyclic diazepines adopt twisted boat-like conformations. Atomic deviations with respect to the plane defined by atoms N1, N2 and C9 in molecule *A* are 0.824 (3), 0.830 (2), 0.389 (3) and 0.921 (3) Å for atoms C1, C6, C7 and C8, respectively. However, atomic deviations with respect to the plane defined by atoms N3, N4 and C52 in molecule *B* are 0.777 (3), 0.785 (2), 0.399 (3) and 0.944 (2) Å for atoms C44, C49, C50 and C51, respectively. The conformations of the oxazinones were determined using the least-squares plane passing through atoms C11, C12 and O3 in molecule *A*, and that passing through atoms C54, C55 and

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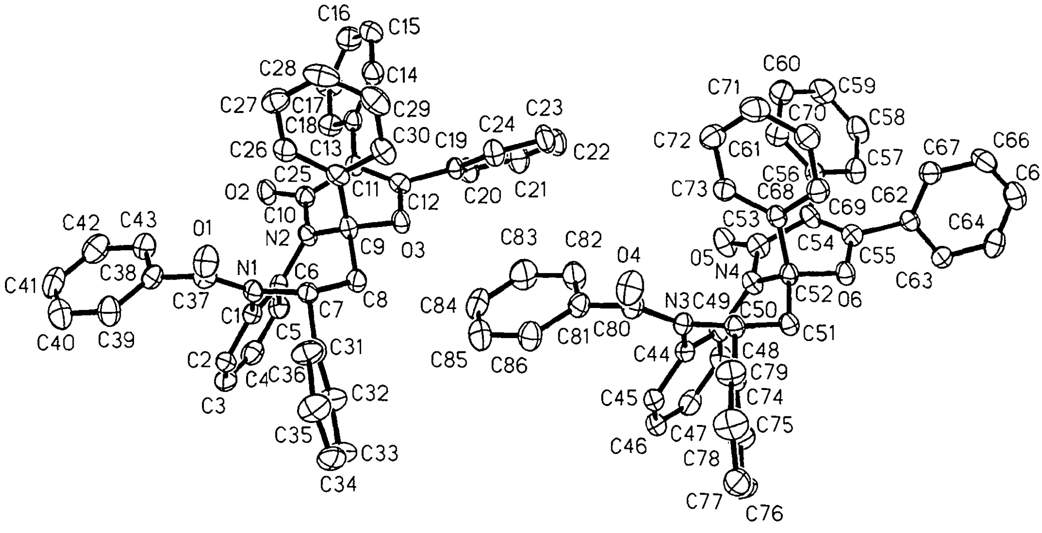

Molecule *A* Molecule *B*

Fig. 1. Perspective view of the two molecules of the title compound with the atom labelling. Displacement ellipsoids are shown at the 30% probability level.

O6 in molecule *B*. Atoms C9 and C52 lie 0.419 (3) and 0.504 (3) Å, respectively, above these planes, and atoms N2 and N4 lie 0.362 (2) and 0.275 (2) Å, respectively, below these planes. Furthermore, the phenyl groups attached to C11 and C12 in molecule *A* adopt a different twist to that of the phenyl groups attached to C54 and C55 in molecule *B*. No significant intermolecular and interatomic contacts could be found.

Experimental

1-Benzoyl-2,4-diphenyl-2,3-dihydro-1*H*-1,5-benzodiazepine (4 mmol) and 2-diazo-1,3-diphenyl-1,3-propanedione (4.4 mmol) (Meier *et al.*, 1986) were dissolved in toluene (10 ml). The mixture was then stirred for 10–15 min at 373 K. Toluene was evaporated at reduced pressure to obtain a brown oil. This material was recrystallized from benzene to yield white crystals of the title compound. The colourless single crystal used for analysis was obtained by evaporation from a saturated ethyl acetate solution of the compound.

Crystal data

$C_{43}H_{32}N_2O_3$
$M_r = 624.71$
Triclinic
$P\bar{1}$
$a = 9.346$ (1) Å
$b = 14.441$ (1) Å
$c = 24.524$ (2) Å
$\alpha = 90.00$ (1)°
$\beta = 97.13$ (1)°
$\gamma = 94.55$ (1)°
$V = 3273.8$ (5) Å^3
$Z = 4$
$D_x = 1.267$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.5$–22.5°
$\mu = 0.080$ mm^{-1}
$T = 293$ (2) K
Plate
0.30 × 0.11 × 0.05 mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: none
12 009 measured reflections
11 508 independent reflections
3903 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.042$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 17$
$l = -29 \rightarrow 29$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.179$
$S = 0.973$
11 503 reflections
866 parameters
H atoms riding, fixed $U_{\rm iso} = 0.080$ Å^2
$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.194$ e Å^{-3}
$\Delta\rho_{\min} = -0.222$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0022 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O3—C12	1.368 (4)	O6—C55	1.374 (4)
O3—C9	1.457 (4)	O6—C52	1.450 (4)
N1—C37	1.367 (4)	N3—C80	1.359 (4)
N1—C1	1.429 (4)	N3—C44	1.435 (4)
N1—C7	1.491 (4)	N3—C50	1.493 (4)
N2—C10	1.401 (4)	N4—C53	1.382 (4)
N2—C9	1.440 (4)	N4—C49	1.446 (4)
N2—C6	1.441 (4)	N4—C52	1.451 (4)
C7—C8	1.532 (4)	C50—C51	1.528 (4)
C8—C9	1.520 (5)	C51—C52	1.520 (5)
C10—C11	1.475 (5)	C53—C54	1.480 (5)
C11—C12	1.351 (5)	C54—C55	1.335 (5)
C12—O3—C9	114.0 (3)	C55—O6—C52	113.0 (3)
C37—N1—C1	122.8 (3)	C80—N3—C44	123.0 (3)

C37—N1—C7	118.3 (3)	C80—N3—C50	116.5 (3)
C1—N1—C7	117.9 (3)	C44—N3—C50	118.9 (3)
C10—N2—C9	117.1 (3)	C53—N4—C49	120.6 (3)
C10—N2—C6	117.9 (3)	C53—N4—C52	116.3 (3)
C9—N2—C6	123.3 (3)	C49—N4—C52	122.6 (3)
C6—C1—N1	118.9 (3)	C49—C44—N3	120.9 (3)
C2—C1—N1	121.5 (3)	C45—C44—N3	120.0 (3)
C1—C6—N2	120.6 (3)	C44—C49—N4	121.1 (3)
N1—C7—C31	111.8 (3)	N3—C50—C74	112.5 (3)
N1—C7—C8	110.4 (3)	N3—C50—C51	110.1 (3)
C31—C7—C8	112.3 (3)	C74—C50—C51	112.1 (3)
C9—C8—C7	114.4 (3)	C52—C51—C50	113.6 (3)
N2—C9—C8	112.5 (3)	O6—C52—C51	103.9 (3)
O3—C9—C8	103.5 (3)	N4—C52—C51	113.2 (3)
N2—C9—C25	112.0 (3)	O6—C52—C68	108.3 (3)
O3—C9—C25	107.9 (3)	N4—C52—C68	110.9 (3)

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1494). Services for accessing these data are described at the back of the journal.

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2,2′-Bibenzoxazole

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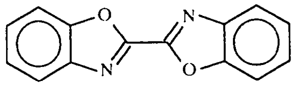
Abstract

In the title compound, $C_{14}H_8N_2O_2$, the oxazole ring systems are in a coplanar configuration. The length of the C—C bond between the benzoxazole units is 1.447 (3) Å. In the five-membered oxazole rings, C1—O = 1.345 (2) Å and C1—N = 1.289 (2) Å.

Comment

The title compound, (I), was obtained after a solution of *mer*-tris(2-trimethylsiloxyphenyl isocyanide)tricarbonylchromium in methanol was exposed to daylight for three weeks. The metal complex decomposes in methanolic solution and 2-trimethylsiloxyphenyl isocyanide is liberated; cyclization of the free ligand results in heterocyclic benzoxazole (Ferris *et al.*, 1973; Fraser *et al.*, 1985). Photodehydrodimerization of this compound yields 2,2′-bibenzoxazole (Grellmann & Tauer, 1974).



(I)

Dense packing of the molecules in the crystal structure is reflected in the stacking distance of 3.34 Å between two molecules.

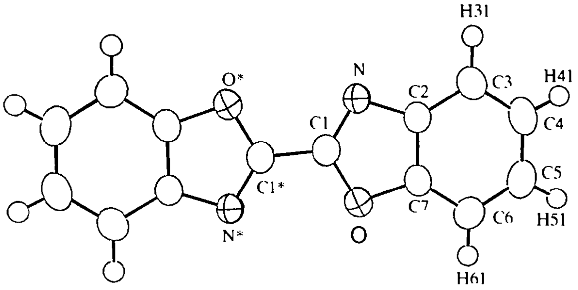


Fig. 1. Plot showing the displacement ellipsoids at the 50% probability level and the atomic numbering scheme. H atoms are shown as small spheres with arbitrary radii. Starred atoms (*) have transformed coordinates $(-x, -y, -z+1)$.

Experimental

Crystals were grown by slow diffusion of hexane into a solution of 2,2-bibenzoxazole in chloroform.

Crystal data

$C_{14}H_8N_2O_2$
$M_r = 236.23$
Monoclinic
$P2_1/n$
$a = 4.644\ (3)$ Å
$b = 16.559\ (5)$ Å
$c = 7.007\ (3)$ Å
$\beta = 94.19\ (4)°$
$V = 537.4\ (4)$ Å^3
$Z = 2$
$D_x = 1.456$ Mg m^{-3}
$D_m = 1.460$ Mg m^{-3}
D_m measured by flotation in $CHCl_3/CH_2Cl_2$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.0–11.5°$
$\mu = 0.101$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.61 × 0.28 × 0.28 mm
Colourless