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9-(4-Methylbenzylidene)-4,8-diphenyl-6-*p*-tolyl-2-oxa-3,7-diazaspiro[4.4]nona-3,7-dien-1-one

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The title compounds, $C_{33}H_{26}N_2O_2$, is the unexpected spiran product of a synthetic reaction. The crystal structure has been determined at room temperature. The skeleton is composed of a spiro[4.4] system formed by an isoxazolone and a substituted pyrroline ring obtained by a series of tandem reactions. The carbonyl group of the isoxazolone ring shows the usual asymmetry of the exocyclic bond angles [121.7 (3) *versus* 130.7 (4)°].

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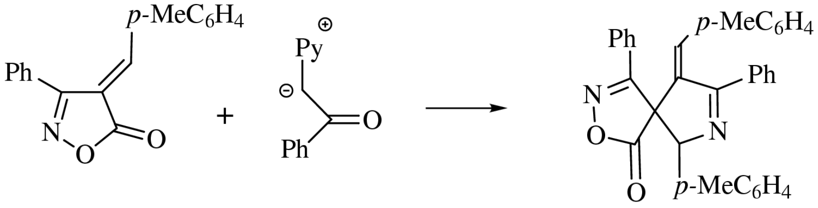
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.049
wR factor = 0.126
Data-to-parameter ratio = 13.7

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

Comment

The formation of the title compound, (I), like the *o*-$MeOC_6H_4$- derivative (Bruno *et al.*, 2001*a*), was rationalized in terms of a series of tandem reactions involving Michael- and retro-Michael reactions, C-alkylation, aldol addition and diastereospecific cyclization (Risitano *et al.*, 2001).



(I)

The stereochemistry around the C═C double bond and the newly created tetrahedral C atoms in the spiro compounds could not easily be established by any spectral technique. Therefore, the present study was undertaken in order to obtain unambiguous structural characterization of this new molecule.

The compound consists of a spiro[4.4] system formed by an isoxazolone and a three-substituted pyrroline rings. The pivot atom C1 of the spiro-center and the C4 pyrroline atom are two chiral centers having the same configuration (*R*,*R* for the molecule depicted in Fig. 1). Since the compound crystallizes in a centrosymmetric space group, in the solid state we have a racemic mixture.

Bond distances and angles are in good agreement with the literature values (Bertolasi *et al.*, 1994; Brehm *et al.*, 1992). Here we observe the usual asymmetry in bond angles around the carbonyl group. This significant asymmetry is systematically present in all 2800 five-membered rings reported in the last release (5.19) of the Cambridge Structural Database (Allen *et al.*, 1991) that contain a carbonyl group as well as in

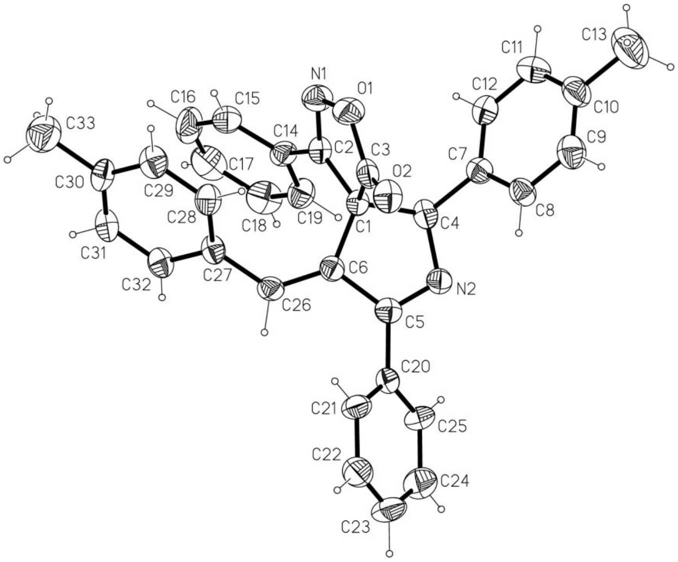


Figure 1
Perspective view of the title compound showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

cumarine derivatives (Bruno *et al.*, 2001*b*). The main discrepancy between the title compound and the *o*-MeO derivative arises from the rotation of the phenyl rings as evidenced by the significant difference of the corresponding torsion angles N1—C2—C14—C15 and C6—C26—C27—C28 of 32.7 (5) and 20.0 (5)°, respectively. All the heteroatoms of the spiro fragments are engaged in some weak intra- and intermolecular hydrogen bonds which determine the relative orientations of substituents with respect to the spiro moiety and the total crystal packing.

Experimental

The title compound was obtained as a single diastereomer from 4-arylmethyleneisoxazol-5-one and an *in situ* prepared *N*-ylide (Risitano *et al.*, 1997) (see reaction Scheme above).

Crystal data

$C_{33}H_{26}N_2O_2$
$M_r = 482.56$
Monoclinic, $P2_1/c$
$a = 10.909$ (3) Å
$b = 18.502$ (7) Å
$c = 13.092$ (4) Å
$\beta = 97.143$ (12)°
$V = 2621.9$ (15) Å^3
$Z = 4$

$D_x = 1.222$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 28 reflections
$\theta = 2.2$–12.5°
$\mu = 0.08$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.46 × 0.27 × 0.22 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
5738 measured reflections
4602 independent reflections
1712 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$

$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 21$
$l = -15 \rightarrow 15$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.126$
$S = 1.14$
4602 reflections
335 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0063 (6)

Table 1
Selected geometric parameters (Å, °).

C3—O2	1.199 (4)	C2—C14	1.479 (4)
C3—O1	1.372 (4)	N1—O1	1.456 (3)
C3—C1	1.522 (4)	C4—N2	1.471 (4)
C1—C2	1.490 (4)	N2—C5	1.298 (4)
C1—C6	1.517 (4)	C5—C6	1.477 (4)
C1—C4	1.612 (4)	C6—C26	1.345 (4)
C2—N1	1.293 (3)	C26—C27	1.468 (4)
O2—C3—O1	121.7 (3)	C6—C1—C3	113.3 (3)
O2—C3—C1	130.7 (4)	C2—C1—C4	113.6 (3)
C2—C1—C6	120.6 (3)	C3—C1—C4	108.9 (3)
C2—C1—C3	99.9 (3)	C6—C26—C27	128.4 (3)
N1—C2—C14—C15	−32.1 (5)	C6—C5—C20—C21	−42.0 (5)
N2—C4—C7—C8	−23.0 (4)	C6—C26—C27—C28	−44.1 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$\cdots$N2	0.93	2.57	2.886 (5)	100
C15—H15$\cdots$N1	0.93	2.56	2.840 (5)	97

Due to the small crystal size, the diffraction data were collected twice at room temperature. A preliminary data collection of a small crystal was collected up to $2\theta = 46°$. The structure determination was carried out using the data of this reduced 2θ shell. When it was possible to obtain larger crystals, a complete data collection was performed up to $2\theta = 50°$ and this was used to refine the structure model. Reflection intensities were evaluated by profile fitting of a 96-step peak scan over 2θ shells procedure (Diamond, 1969) and then corrected for Lorentz–polarization effects. Standard uncertainties $\sigma(I)$ were estimated from counting statistics. H atoms have been located at idealized positions and were allowed to ride on their parent C atoms with a unique fixed isotropic displacement parameter (0.08 Å^2).

Data collection: *XSCANS* (Bruker, 1999); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XPW* (Siemens, 1996); software used to prepare material for publication: *PARST*97 (Nardelli, 1995) and *SHELXL*97.

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