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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
R factor = 0.051
wR factor = 0.154
Data-to-parameter ratio = 17.1

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

(-)-(3a'S,4'S,9b'S,1R,2S,5R)-4'-Ethyl-3a',4',5',7',8',9b'-hexahydro-2-isopropyl-5-methyl-2'-phenylspiro[cyclohexane-1,7'-dioxino[3,2-e]isoindole]-1',3',9'-trione

The title compound, $\text{C}_{27}\text{H}_{33}\text{NO}_5$, obtained from diethyl ether, crystallizes in space group $P2_1$ with four molecules in the asymmetric unit. The dioxinone and imide rings are almost planar, whereas the cyclohexane and cyclohexene rings form distorted conformations. The crystal structure confirms an earlier proposal about the stereoselectivity of Diels–Alder reactions to spirocyclic chiral 1,3-dienes.

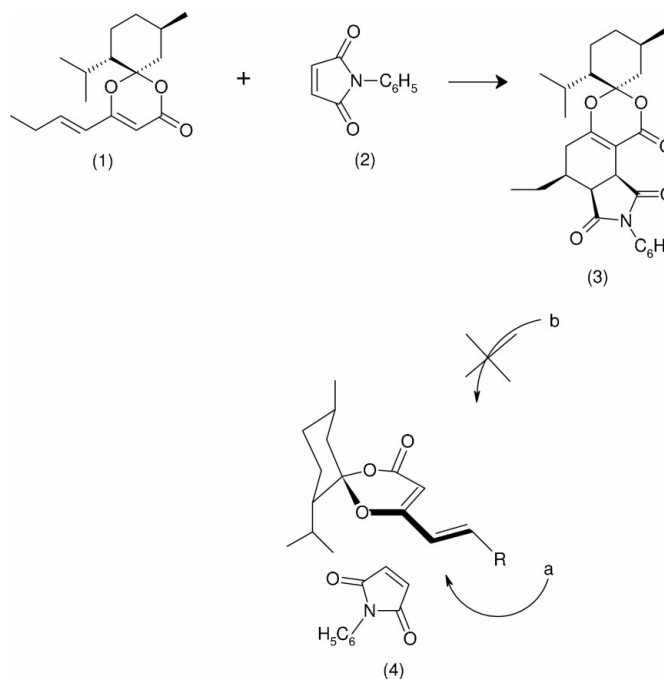
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Comment

Recently, we reported on highly diastereoselective Diels–Alder reactions of spirocyclic chiral dienes derived from diketene–(–)-menthone adducts (Hoffmann & Mattay, 1995). For example, the enantiomerically pure diene (1) quantitatively yields the title compound, (3), upon reaction of *N*-phenylmaleinimide, NPM, (2), under high-pressure conditions. On the basis of NMR studies and molecular models, an *endo* attack from the less hindered *a* side was proposed, leading to (4), supporting the selectivity model discussed in detail by Graalfs *et al.* (1999).



We now report an X-ray crystal structure analysis that fully supports our earlier proposal. Crystals of (3) precipitated at 278 K from a solution in diethyl ether. Preliminary methods (Weissenberg and precession photographs) indicated the orthorhombic space group $P2_12_12_1$. The intensity in every

second layer perpendicular to the a axis was rather weak, indicating the presence of a superstructure in this direction. Nevertheless, structure solution in this space group failed. In the monoclinic space group $P2_1$, structure solution and refinement succeeded with four independent molecules ($A-D$) in the asymmetric unit. Two pairs, (A,D) and (B,C), are related by translation of approximately $a/2$. A non-crystallographic twofold axis parallel to a at approximately $y = 0.12$, $z = \frac{1}{4}$, with a translation of approximately $a/4$, generates the other pairs, (A,B) and (C,D). Structure refinement converged with $wR_2 = 0.36$ ($R_1 = 0.11$). The fact that the β angle is close to 90° indicates the possibility of a twinned crystal. Introducing the twin law matrix $1\ 0\ 0 / 0\ \bar{1}\ 0 / 0\ 0\ \bar{1}$ improves the refinement, with a twin ratio of 0.505:0.495 (1). The geometric parameters of the four independent molecules are almost equal and in the normal ranges.

Experimental

The title compound was obtained by slow evaporation from a diethyl ether solution.

Crystal data

$C_{27}H_{33}NO_5$	$D_x = 1.200\ \text{Mg m}^{-3}$
$M_r = 451.54$	Cu $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 14.3100$ (10) Å	$\theta = 36-45^\circ$
$b = 13.1112$ (5) Å	$\mu = 0.66\ \text{mm}^{-1}$
$c = 26.642$ (2) Å	$T = 293$ (2) K
$\beta = 90.007$ (5)°	Block, colourless
$V = 4998.6$ (5) Å ³	$0.80 \times 0.39 \times 0.27\ \text{mm}$
$Z = 8$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 75.1^\circ$
$\omega/2\theta$ scans	$h = -17 \rightarrow 16$
Absorption correction: none	$k = -16 \rightarrow 16$
22 636 measured reflections	$l = -33 \rightarrow 33$
20 376 independent reflections	3 standard reflections
16 110 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{\text{int}} = 0.022$	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0926P)^2 + 0.2501P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.154$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.44\ \text{e Å}^{-3}$
20 376 reflections	$\Delta\rho_{\text{min}} = -0.19\ \text{e Å}^{-3}$
1190 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	9618 Friedel pairs
	Flack parameter: 0.02 (14)

H atoms were refined using a riding model [$C-H = 0.93-0.98$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$].

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Shel-

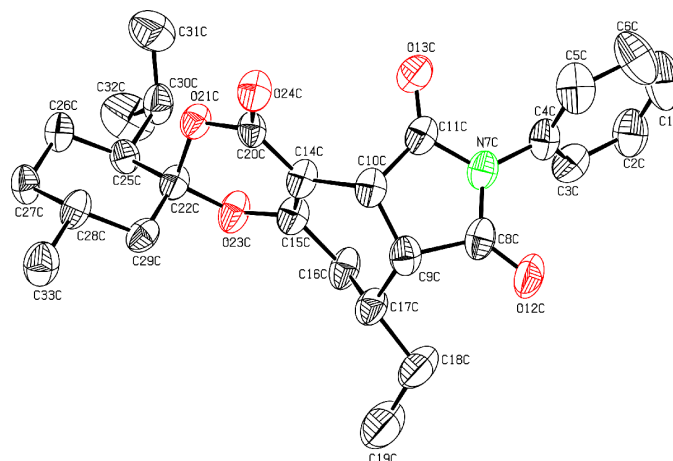


Figure 1
ORTEP (Johnson, 1976) view of one molecule of (3). Displacement ellipsoids are shown at the 40% probability level. H atoms have been omitted for clarity.

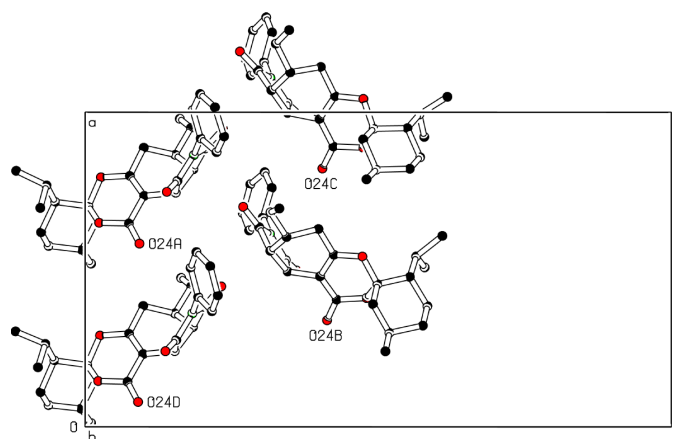


Figure 2
The four independent molecules in the asymmetric unit, viewed along the b axis. H atoms have been omitted for clarity.

drick, 1997); molecular graphics: *ORTEP* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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