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4-Methoxy-4a-nitro-9-(phenylsulfonyl)-4,4a,9,9a-tetrahydro-1*H*-carbazol-2(3*H*)-one

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Key indicators

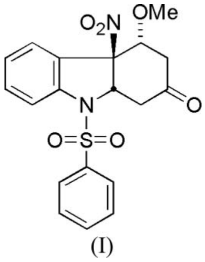
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.015 Å
R factor = 0.055
wR factor = 0.255
Data-to-parameter ratio = 13.1

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

The crystal structure of the title molecule, $C_{19}H_{18}N_2O_6S$, confirms the structure of this novel Diels–Alder adduct formed from the reaction of 3-nitro-1-(phenylsulfonyl)indole and 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Danishefsky's diene). The angle between the planes of the indoline ring system and the phenylsulfonyl ring is 69.9 (4)°.

Comment

We have found that both 2- and 3-nitroindoles undergo Diels–Alder cycloaddition reactions to afford a simple synthesis of carbazoles (Kishbaugh & Gribble, 2001). Surprisingly, the reaction between 3-nitro-1-(phenylsulfonyl)indole and 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Danishefsky's diene) provided the title initial cycloadduct, 4-methoxy-4a-nitro-9-(phenylsulfonyl)-4,4a,9,9a-tetrahydro-1*H*-carbazol-2(3*H*)-one, (I), as the major product, rather than the expected 2-hydroxy-9-(phenylsulfonyl)carbazole, which was the minor product. The observed regiochemistry of the present Diels–Alder reaction is consistent with the known reactivity of Danishefsky's diene with nitroalkenes in normal electron-demand reactions (Node *et al.*, 1996), but the observed *exo* mode of addition, affording a *trans* arrangement of nitro and methoxyl groups, rather than an *endo* mode of addition, was not necessarily expected. We now describe the crystal structure of (I).



(I)

The X-ray crystallographic analysis confirms the molecular structure and atom connectivity for (I) (Fig. 1) that we had proposed for this compound based on NMR spectroscopy (Kishbaugh & Gribble, 2001). The ketone carbonyl C2—O3 bond is 1.206 (13) Å, which is normal for a cyclohexanone [1.24 (2) Å; Romers, 1956], and the C1—C2—C3 bond angle of 114.4 (8)° compares with the electron diffraction value of 117 (3)° for cyclohexanone (Romers, 1956). The angle between the planes of the indoline ring system and the phenylsulfonyl ring is 69.9 (4)°. The phenylsulfonyl group is oriented away from the cyclohexanone ring and is disposed towards the nitro group, while the methoxyl group adopts an equatorial position on the cyclohexanone ring. The sum of the bond angles surrounding the indoline N atom (N1) is 346.3°, indicating pyramidal stereochemistry.

Experimental

3-Nitro-1-(phenylsulfonyl)indole (187 mg, 0.62 mmol) (Pelkey & Gribble, 1999) and commercially available *trans*-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (0.2 ml, 0.93 mmol) in toluene (12 ml) were heated to reflux for 36 h and allowed to cool to room temperature. The toluene was removed by rotary evaporation. The resulting amorphous solid was dissolved in tetrahydrofuran (10 ml) and 10% aqueous HCl (5 ml) and stirred for 3 h. After removal of tetrahydrofuran by rotary evaporation, the solution was neutralized by the addition of 5% aqueous $NaHCO_3$ and extracted with dichloromethane (4 × 20 ml). The combined organic layers were washed with brine (20 ml), dried (Na_2SO_4) and concentrated, to yield a brown oil. This was purified by column chromatography (silica gel; hexanes–ethyl acetate, 2:1 *v*/*v*) to yield the title compound as a white solid (127 mg, 56%; m.p. 451–452 K). IR (film): ν_{max} 1722 (C═O), 1361 (SO_2), 1166 (SO_2) cm^{-1}. Analysis, calculated for $C_{19}H_{18}N_2O_6S$: C 56.71, H 4.51, N 6.96, S 7.97%; found: C 56.40, H 4.45, N 6.88, S 7.91%. Recrystallization from diethyl ether yielded crystals of (I) suitable for X-ray crystallography.

Crystal data

$C_{19}H_{18}N_2O_6S$
$M_r = 402.41$
Orthorhombic, *Pbca*
$a = 23.352$ (6) Å
$b = 15.085$ (14) Å
$c = 10.952$ (9) Å
$V = 3858$ (5) Å^3
$Z = 8$
Mo *Kα* radiation
$\mu = 0.21$ mm^{-1}
$T = 296$ K
0.40 × 0.40 × 0.20 mm

Data collection

Rigaku AFC-6*S* diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.922$, $T_{max} = 0.960$
3333 measured reflections
3333 independent reflections
780 reflections with $I > 2\sigma(I)$
3 standard reflections every 150 reflections intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.255$
$S = 0.93$
3333 reflections
255 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

The H atoms were included in the riding-model approximation, with C—H = 0.93–0.98 Å, and with $U_{iso}(H) = 1.2–1.3U_{eq}(C)$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

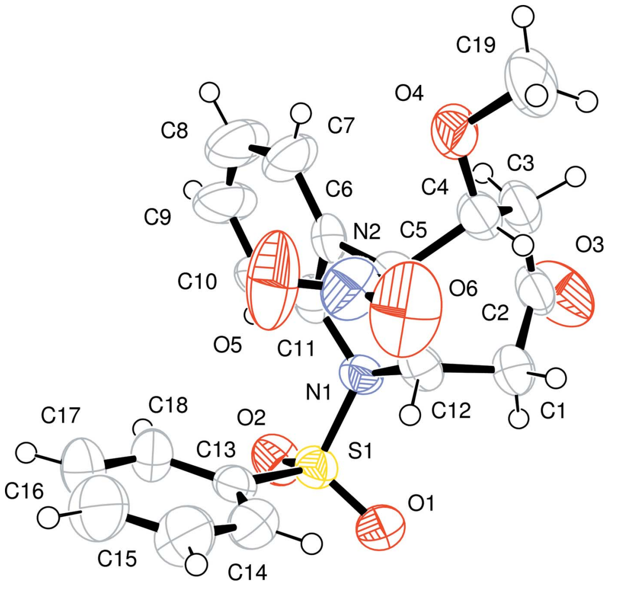


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and with 50% probability displacement ellipsoids.

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