

The nature of the 2 + 2' functional group and the cone conformation were deduced initially from solution ^1H NMR: two *tert*-butyl singlets at 1.04 and 1.13 p.p.m., and a single *AB* system for the bridging methylene groups at 3.16 and 4.69 p.p.m. ($J_{AB} = 12.7$ Hz).

The structure was solved by direct methods using 499 reflections with $E > 2.0$ in *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), and anisotropic full-matrix refinement on F using *SHELX76* (Sheldrick, 1976). A Lorentz-polarization correction was applied. Phenyl H atoms were inserted at calculated positions; every methyl group was treated as a rigid CH_3 unit with its original orientation taken from the strongest H-atom peak in a difference Fourier synthesis; other H atoms were found by difference synthesis and theoretically adjusted. No H atoms were refined. All calculations were performed on a MicroVAX II.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71234 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1034]

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Acta Cryst. (1993). **C49**, 2124–2126

Structure of a Phenylsulfonyllallene

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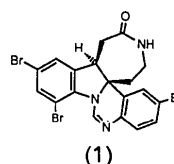
(Received 3 February 1993; accepted 26 May 1993)

Abstract

The crystal structure of 2-phenyl-3-[2-(phenylsulfonyl)-2,3-butadien-1-yl]indole (2) shows that reaction of the Grignard derivative of 2-phenylindole with 2,3-diphenylsulfonylbuta-1,3-diene involves nucleophilic addition to the latter, with loss of phenylsulfinate, producing an allene.

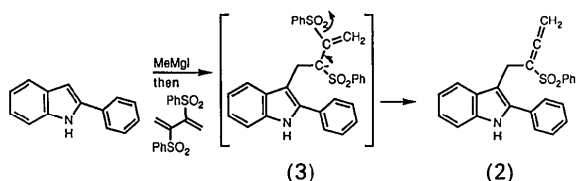
Comment

We are developing a synthetic route to the marine alkaloid hinckdentine (1) (Blackman, Hambley, Picker, Taylor & Thirasasana, 1987), and were seeking to establish a tricyclic nucleus containing both



the required 2,3-dihydroindole and a 2-aryl substituent, following the methodology recently described (Bäckvall, Plobeck, & Juntenen, 1989; Bäckvall & Plobeck, 1990), whereby the Grignard derivatives of indole, and 2-methylindole, undergo a cycloaddition with 2-phenylsulfonyl-1,3-butadiene. Unfortunately, we found that no reaction took place with 2-phenylindole and in seeking to encourage a comparable transformation we turned to the more electrophilic diene, 2,3-diphenylsulfonylbuta-1,3-diene (Jegathan & Okamura, 1982). Reaction of this with the Grignard derivative of 2-phenylindole led to an indolic, rather than a 2,3-dihydroindolic, product which was crystallized and for which the allenic

structure (2) was determined by X-ray crystallography. Crystallization from methanol led to twinned crystals but a recrystallization from chloroform provided a sample (m.p. 451–453 K) which was suitable for X-ray analysis. The formation of (2) can be easily rationalized, the expulsion of phenylsulfinate [arrows on (3) in scheme below] being either a second step, as shown, or perhaps synchronous with the indolyl Grignard addition. Subsequent to our work, the isolation of a comparable phenylsulfonylallene from a reaction of indole with 2,3-diphenylsulfonylbuta-1,3-diene was described (Padwa, Gareau, Harrison & Rodriguez, 1992).



The asymmetric unit consists of two crystallographically unrelated molecules, *A* and *B*. Since their geometries are very similar, only parameters for molecule *B* have been included in this paper. However, all parameters for both molecules *A* and *B* have been deposited.

The phenyl substituent in (2) lies at a torsional angle of 45° with respect to the planar indole. Short intermolecular contacts between the indolic N atoms and one of the O atoms of the phenylsulfonyl groups indicate hydrogen-bonding interactions between molecules *A* and *B*. An examination of the Cambridge Structural Database (1992) revealed the crystal structures of more than 40 other allenes; however,

this present determination is the first of an allene which carries a phenylsulfonyl substituent. It is very interesting that the phenylsulfonyl-bearing allenic double bond [1.300 (5) Å] is effectively exactly the same length as the other allenic bond [1.301 (6) Å] indicating only a marginal conjugative influence by the sulfonyl substituent.

Experimental

Crystal data

C₂₄H₁₉NO₂S

M_r = 385.48

Monoclinic

*P*2₁/*c*

a = 20.666 (2) Å

b = 10.710 (1) Å

c = 20.302 (3) Å

β = 118.720 (8)°

V = 3941 (2) Å³

Z = 8

D_x = 1.299 Mg m^{−3}

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 19

reflections

θ = 39–40°

μ = 1.565 mm^{−1}

T = 295 (1) K

Block

0.60 × 0.50 × 0.50 mm

Colourless

Data collection

Rigaku AFC-5R diffractometer

ω/2θ scans

Absorption correction:

empirical (*DIFABS*;

Walker & Stuart, 1983)

T_{min} = 0.44, *T_{max}* = 1.17

6436 measured reflections

6234 independent reflections

4616 observed reflections

[*I* > 3.0σ(*I*)]

R_{int} = 0.042

θ_{max} = 60°

h = −23 → 22

k = −4 → 12

l = −8 → 22

3 standard reflections

monitored every 150

reflections

intensity variation: none

Refinement

Refinement on *F*

R = 0.057

wR = 0.080

S = 2.62

4616 reflections

505 parameters

H-atom parameters not refined

w = 4*F_o*²/σ²(*F_o*²)

(Δ/σ)_{max} < 0.01

Δρ_{max} = 0.27 e Å^{−3}

Δρ_{min} = −0.25 e Å^{−3}

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

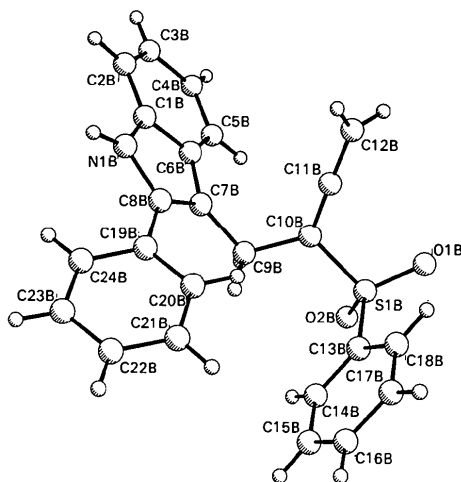


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of 2-phenyl-3-[2-(phenylsulfonyl)-2,3-butadien-1-yl]indole (2) showing the numbering scheme.

The H atoms attached to C atoms were placed in calculated positions (C—H = 0.95 Å), while those attached to N atoms were found by difference Fourier methods. All were given isotropic temperature factors of 1.2 times the *B_{eq}* value of the atom to which they were bonded. Neutral-atom scattering factors were taken from Cromer & Waber (1974); anomalous dispersion effects were included in *F_{calc}* (Ibers & Hamilton, 1964). Computer programs used were *MITHRIL* (Gilmore, 1984), *DIRDIF* (Parthasarathi, Beurskens & Slot, 1983), *TEXSAN* (Molecular Structure Corporation, 1985) and *PLUTO* (Motherwell & Clegg, 1978).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

	x	y	z	B_{eq}
S1B	0.23005 (5)	0.1739 (1)	0.11781 (5)	3.92 (4)
O1B	0.2918 (1)	0.2306 (3)	0.1160 (2)	5.1 (1)
O2B	0.2390 (2)	0.0546 (3)	0.1520 (2)	5.6 (1)
N1B	-0.0771 (2)	0.1314 (3)	-0.1716 (2)	4.1 (1)
C1B	-0.0395 (2)	0.0459 (4)	-0.1899 (2)	4.0 (2)
C2B	-0.0579 (2)	-0.0110 (5)	-0.2581 (2)	5.1 (2)
C3B	-0.0101 (3)	-0.1024 (5)	-0.2582 (3)	5.7 (2)
C4B	0.0548 (2)	-0.1322 (4)	-0.1931 (3)	5.3 (2)
C5B	0.0735 (2)	-0.0721 (4)	-0.1265 (3)	4.8 (2)
C6B	0.0264 (2)	0.0195 (4)	-0.1242 (2)	3.8 (2)
C7B	0.0278 (2)	0.0947 (4)	-0.0657 (2)	3.5 (1)
C8B	-0.0371 (2)	0.1628 (4)	-0.0965 (2)	3.8 (2)
C9B	0.0879 (2)	0.0932 (4)	0.0141 (2)	4.1 (2)
C10B	0.1557 (2)	0.1654 (4)	0.0255 (2)	3.5 (1)
C11B	0.1648 (2)	0.2208 (4)	-0.0265 (2)	4.2 (2)
C12B	0.1767 (2)	0.2730 (6)	-0.0776 (3)	6.8 (2)
C13B	0.1971 (2)	0.2780 (4)	0.1622 (2)	4.0 (2)
C14B	0.1565 (2)	0.2332 (5)	0.1943 (2)	5.7 (2)
C15B	0.1286 (3)	0.3196 (8)	0.2262 (3)	7.6 (3)
C16B	0.1426 (3)	0.4431 (8)	0.2258 (3)	8.2 (3)
C17B	0.1834 (3)	0.4860 (6)	0.1942 (3)	7.4 (3)
C18B	0.2099 (2)	0.4047 (5)	0.1612 (3)	5.3 (2)
C19B	-0.0674 (2)	0.2434 (4)	-0.0596 (2)	3.8 (2)
C20B	-0.0243 (2)	0.3257 (4)	-0.0022 (3)	5.2 (2)
C21B	-0.0531 (3)	0.3908 (5)	0.0355 (3)	6.2 (2)
C22B	-0.1270 (3)	0.3800 (5)	0.0144 (3)	6.3 (2)
C23B	-0.1706 (3)	0.3014 (5)	-0.0423 (3)	5.5 (2)
C24B	-0.1414 (2)	0.2330 (4)	-0.0791 (2)	4.4 (2)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

S1B—O1B	1.430 (3)	C7B—C8B	1.383 (5)
S1B—O2B	1.424 (3)	C7B—C9B	1.495 (5)
S1B—C10B	1.764 (4)	C8B—C19B	1.466 (5)
S1B—C13B	1.764 (4)	C9B—C10B	1.519 (5)
N1B—C1B	1.365 (5)	C10B—C11B	1.300 (5)
N1B—C8B	1.382 (5)	C11B—C12B	1.301 (6)
C1B—C2B	1.387 (6)	C19B—C20B	1.389 (6)
C1B—C6B	1.403 (5)	C19B—C24B	1.388 (5)
C2B—C3B	1.393 (6)	C20B—C21B	1.365 (6)
C3B—C4B	1.394 (6)	C21B—C22B	1.378 (7)
C4B—C5B	1.375 (6)	C22B—C23B	1.361 (7)
C5B—C6B	1.397 (6)	C23B—C24B	1.375 (6)
C6B—C7B	1.425 (5)		
N1B—C1B—C6B	107.2 (3)	C10B—C11B—C12B	177.3 (5)
C2B—C1B—C6B	122.4 (4)	S1B—C13B—C14B	119.7 (4)
C1B—C2B—C3B	117.1 (4)	S1B—C13B—C18B	119.2 (3)
C2B—C3B—C4B	121.3 (4)	C8B—C19B—C20B	122.9 (4)
C3B—C4B—C5B	120.9 (4)	C8B—C19B—C24B	119.3 (4)
C4B—C5B—C6B	119.3 (4)	C20B—C19B—C24B	117.7 (4)
C1B—C6B—C5B	118.9 (4)	C19B—C20B—C21B	121.2 (4)
C1B—C6B—C7B	107.4 (3)	C20B—C21B—C22B	119.9 (5)
C5B—C6B—C7B	133.6 (4)	C21B—C22B—C23B	120.0 (5)
C6B—C7B—C8B	107.2 (3)	C22B—C23B—C24B	120.3 (4)
C6B—C7B—C9B	124.8 (3)	C19B—C24B—C23B	120.9 (4)
C8B—C7B—C9B	128.0 (4)	O1B—S1B—O2B	119.0 (2)
N1B—C8B—C7B	107.9 (4)	O1B—S1B—C10B	109.1 (2)
N1B—C8B—C19B	122.0 (3)	O1B—S1B—C13B	108.3 (2)
C7B—C8B—C19B	129.7 (4)	O2B—S1B—C10B	108.3 (2)
C7B—C9B—C10B	112.6 (3)	O2B—S1B—C13B	108.0 (2)
S1B—C10B—C9B	117.2 (3)	C10B—S1B—C13B	102.9 (2)
S1B—C10B—C11B	116.5 (3)	C1B—N1B—C8B	110.3 (3)
C9B—C10B—C11B	126.3 (3)	N1B—C1B—C2B	130.4 (4)

We thank the SERC, UK, for funds for the purchase of the Rigaku AFC-5R diffractometer, and the SERC and SmithKline Beecham Pharmaceuticals for a CASE studentship (NB).

Lists, for both molecules A and B, of structure factors, anisotropic thermal parameters, H-atom coordinates, complete intermolecular distances including H atoms, and torsion angles, and positional parameters for Molecule A have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71360 (69 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1050]

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Acta Cryst. (1993). **C49**, 2126–2128

Structure of [2]Benzoxepino[4,3-*b*]indole

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(Received 5 January 1993; accepted 29 April 1993)

Abstract

The crystal structure of [2]benzoxepino[4,3-*b*]indole, (2), shows that this tetracyclic molecule comprises two essentially flat 'wings', the indole and benzene aromatic moieties, linked *via* a 'hinge' comprising the CH_2O and carbonyl groups, and producing a butterfly shape; the angle between the wings is $29.2 (7)^\circ$.