ordinates have not been published (Blessing & Detilta, 1979; Gilardi, 1982; Pierrot, Baldy, Wimmer, Gallo & Boileau, 1985).

Experimental

Glycoluril was purchased from Aldrich and was used without further purification. Crystals were grown by the slow cooling of a filtered hot aqueous solution. The (010) face is predominant and shows perfect cleavage. This observation is consistent with the sheet-like arrangement of the structure (see Fig. 2).

Crystal data

$C_4H_6N_4O_2$
$M_r = 142.12$
Orthorhombic
Cmcm
$a = 7.373\ (2)$ Å
$b = 7.546\ (3)$ Å
$c = 10.579\ (3)$ Å
$V = 588.6\ (3)$ Å^3
$Z = 4$
$D_x = 1.604$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 4$–$13.5°$
$\mu = 0.131$ mm^{-1}
$T = 299$ K
Prism
1.0 × 0.4 × 0.4 mm
Colorless

Data collection

Siemens *R*3*m*/*V* diffractometer
Wyckoff scans
Absorption correction: none
550 measured reflections
486 independent reflections
403 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.0165$
$\theta_{\max} = 29.94°$
$h = -1 \rightarrow 10$
$k = 0 \rightarrow 10$
$l = -14 \rightarrow 0$
3 standard reflections monitored every 197 reflections intensity variation: 0.35%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0405$
$wR(F^2) = 0.1163$
$S = 1.114$
486 reflections
31 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.0785P)^2 + 0.1473P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.268$ e Å^{-3}
$\Delta\rho_{\min} = -0.264$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0	0.2245 (2)	0.46658 (11)	0.0393 (4)
N2	0.14924 (12)	0.3510 (2)	0.63534 (9)	0.0358 (3)
C3	0.1059 (2)	0.4450 (2)	3/4	0.0274 (4)
C4	0	0.3016 (2)	0.57014 (15)	0.0285 (4)

Table 2. *Selected geometric parameters* (Å, °)

O1—C4	1.241 (2)	C3—C3$^{\text{i}}$	1.561 (3)
N2—C4	1.3512 (13)	C4—N2$^{\text{ii}}$	1.3512 (13)
N2—C3	1.4409 (13)		
C4—N2—C3	112.64 (11)	O1—C4—N2	125.47 (7)
N2$^{\text{iii}}$—C3—N2	114.67 (13)	N2—C4—N2$^{\text{ii}}$	109.05 (14)
N2$^{\text{iii}}$—C3—C3$^{\text{i}}$	102.82 (7)		

Symmetry codes: (i) $-x, y, \frac{3}{2} - z$; (ii) $-x, y, z$; (iii) $x, y, \frac{3}{2} - z$.

Data collection, cell refinement and data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*b*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SHELXTL-Plus*.

This work was supported by National Institutes of Health grant GM38575.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: KA1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 3-Phenylsulfinyl-1-phenylsulfonylindole

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Abstract

The title compound 2-(3,4-dihydro-2*H*-pyrrol-5-yl)-1-phenylsulfonylindol-3-yl phenyl sulfoxide, $C_{24}H_{20}N_2O_3S_2$, was isolated, together with 3-chloro-2-(3,4-dihydro-2*H*-pyrrol-5-yl)-1-phenylsulfonylindole, from the treatment of 2-(3,4-dihydro-2*H*-pyrrol-5-yl)indole with sodium hydride and phenylsulfonylchloride, showing that the latter can act as an electrophilic chlorinating agent and as a source of an electrophilic phenylsulfinylating species.

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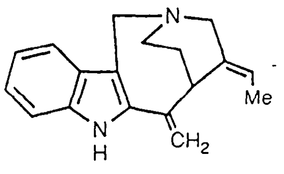
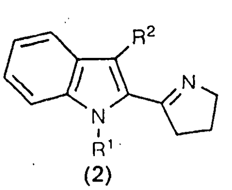
Comment

We are developing a synthetic route (Allen, Bishop, Harris, Hignett, Scopes, Wilson & Joule, 1980) to the indole alkaloid apparicine, (1) (Joule, Monteiro, Durham, Gilbert & Djerassi, 1965), and required the 1-phenylsulfonylindole (2*b*). It seemed possible that this could be obtained from compound (2*a*) (Street, Harris, Bishop, Heatley, Beddoes, Mills & Joule, 1987) using a base to remove the indolic *N*-H atom followed by reaction with phenylsulfonyl chloride; when sodium hydride in dimethylformamide at room temperature was used together with a molar equivalent of phenylsulfonyl chloride, the desired compound (2*b*) was indeed obtained, in 14% yield. This was accompanied by two other products, one of which was shown by spectroscopic analysis to be the 3-chloro analogue (2*c*) (15%), and the other (5%), a compound of m.p. 474–476 K containing two S atoms, was shown by the crystal structure determination described herein to be the sulfone (2*d*).



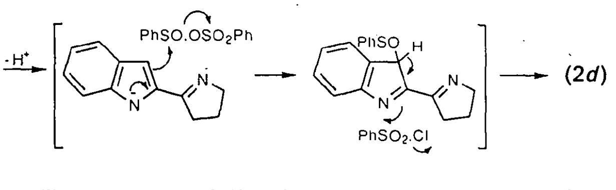
(1)



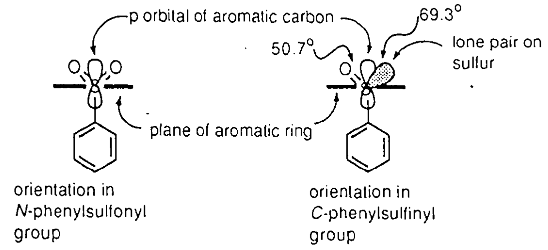
(2)

	R^1	R^2
(*a*)	H	H
(*b*)	$SO_2.Ph$	H
(*c*)	$SO_2.Ph$	Cl
(*d*)	$SO_2.Ph$	SO.Ph

We have observed previously (Dalton, Humphrey, Cooper & Joule, 1983) that treatment of some 2-arylindoles with phenylsulfonyl chloride under phase-transfer conditions leads to 3-chloro-1-phenylsulfonylindoles and that this involves the reagent acting as an electrophilic chlorinating agent. This same process must occur in the present case, producing (2*c*) after a subsequent *N*-phenylsulfonylation; however, we envisage that, in addition, the chlorination by-product, phenylsulfinate, then reacts with excess phenylsulfonyl chloride to produce a mixed sulfonate/sulfinate anhydride: $PhSO_2^- + PhSO_2Cl \rightarrow PhSO.OSO_2.Ph + Cl^-$. This anhydride then acts as a sulfinylating agent, attacking an indolyl anion at the 3 position and eventually leading to (2*d*); the proposed sequence of events is summarized in the scheme below.



The structure of (2*d*) is shown in Fig. 1. The five-membered ring is oriented nearly orthogonal (88.3°) to the indole, presumably to minimize interaction with the two flanking substituents. The orientation of the *N*-phenylsulfonyl group relative to the indolic N atom in (2*d*) is exactly comparable to that found in a previous detailed examination of examples of this unit (Beddoes, Dalton, Joule, Mills, Street & Watt, 1986). The orientation of the sulfoxide is interesting in that the plane of the indole nearly bisects the angle between the sulfoxide O atom and the aromatic C atom linked to the S atom; this implies that the residual sulfur lone pair lies effectively in the plane of the aromatic indole, allowing no overlap between it and the indole π system. The orientation adopted by the sulfoxide is very similar to the orientations adopted by *N*-phenylsulfonylindoles where each of the attached aromatic *p* orbitals is aligned in such a way as to bisect the angles between the sulfur O atoms. In the case of the sulfoxide, assuming the sulfoxide O atom and the lone pair are oriented symmetrically with respect to the S atom, the angles subtended by the indolic C3 *p* orbital with the O atom and the lone pair are 50.7 and 69.3°, respectively.



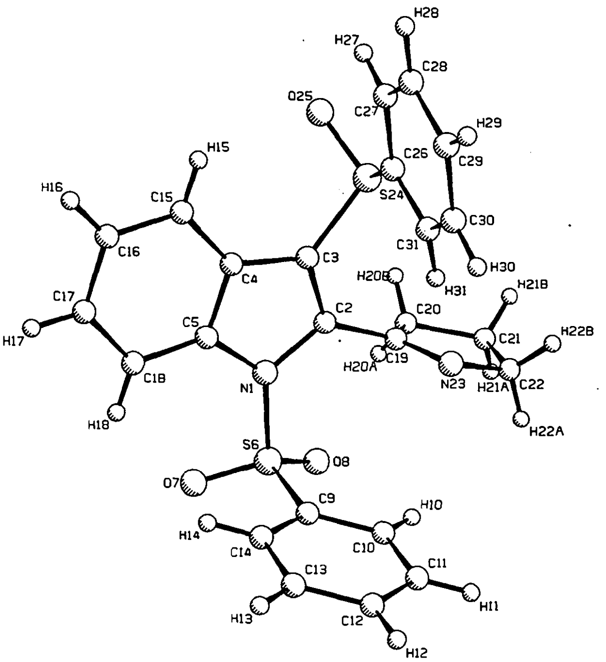


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of sulfone (2*d*) showing the atom-numbering scheme used.

Experimental

The compound was obtained by reaction of 2-(3,4-dihydro-2*H*-pyrrol-5-yl)indole with phenylsulfonyl chloride and sodium hydride in dimethylformamide at room temperature, followed by chromatographic separation of the products, then crystallization from toluene.

Crystal data

$C_{24}H_{20}N_2O_3S_2$
$M_r = 448.55$
Monoclinic
$P2_1/c$
$a = 10.065$ (5) Å
$b = 15.372$ (3) Å
$c = 14.488$ (3) Å
$\beta = 107.25$ (3)°
$V = 2141$ (1) Å^3
$Z = 4$
$D_x = 1.391$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 15 reflections
$\theta = 30$–37°
$\mu = 2.45$ mm^{-1}
$T = 295$ K
Prismatic
0.35 × 0.30 × 0.20 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.70$, $T_{\max} = 1.00$
3558 measured reflections
3347 independent reflections
2287 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.184$
$\theta_{\max} = 60°$
$h = -4 \rightarrow 11$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 15$
3 standard reflections monitored every 150 reflections intensity variation: −1.6%

Refinement

Refinement on *F*
$R = 0.062$
$wR = 0.077$
$S = 2.30$
2287 reflections
280 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
N1	0.6818 (4)	0.1653 (2)	0.2243 (2)	3.9 (2)
C2	0.6875 (5)	0.2211 (3)	0.3015 (3)	3.8 (2)
C3	0.5617 (5)	0.2212 (3)	0.3183 (3)	4.0 (2)
C4	0.4709 (5)	0.1645 (3)	0.2494 (3)	4.1 (2)
C5	0.5469 (5)	0.1291 (3)	0.1933 (3)	4.1 (2)
S6	0.8203 (1)	0.13448 (8)	0.19005 (8)	4.41 (5)
O7	0.7646 (4)	0.1020 (2)	0.0944 (2)	5.8 (2)
O8	0.9130 (4)	0.2062 (2)	0.2093 (3)	6.1 (2)
C9	0.8945 (5)	0.0489 (3)	0.2666 (3)	4.4 (2)
C10	1.0099 (6)	0.0638 (4)	0.3441 (4)	6.2 (3)
C11	1.0686 (7)	−0.0056 (6)	0.4032 (5)	8.0 (4)
C12	1.0126 (9)	−0.0873 (6)	0.3825 (6)	8.0 (4)
C13	0.9003 (7)	−0.1013 (4)	0.3051 (6)	7.2 (3)
C14	0.8387 (5)	−0.0330 (4)	0.2464 (4)	5.7 (3)
C15	0.3310 (5)	0.1416 (3)	0.2325 (4)	5.1 (2)
C16	0.2721 (5)	0.0844 (4)	0.1594 (4)	5.7 (3)
C17	0.3505 (6)	0.0499 (4)	0.1040 (4)	5.8 (3)
C18	0.4876 (6)	0.0711 (3)	0.1185 (4)	5.2 (2)
C19	0.8128 (5)	0.2702 (3)	0.3582 (3)	3.9 (2)
C20	0.8458 (6)	0.3599 (4)	0.3317 (4)	6.2 (3)
C21	0.9692 (8)	0.3832 (5)	0.4194 (5)	9.5 (4)
C22	1.0004 (6)	0.3032 (5)	0.4752 (4)	6.8 (3)
N23	0.8915 (4)	0.2380 (3)	0.4345 (3)	5.0 (2)
S24	0.5242 (1)	0.2896 (1)	0.4048 (1)	5.53 (6)
O25	0.3866 (4)	0.3293 (3)	0.3606 (3)	7.9 (2)
C26	0.5000 (5)	0.2066 (3)	0.4858 (4)	4.9 (2)
C27	0.3842 (7)	0.2093 (5)	0.5143 (6)	8.3 (4)
C28	0.367 (1)	0.1509 (6)	0.5803 (9)	11.5 (6)
C29	0.466 (1)	0.0900 (6)	0.6200 (5)	9.4 (5)
C30	0.5811 (8)	0.0898 (6)	0.5909 (5)	10.0 (5)
C31	0.6006 (7)	0.1490 (5)	0.5263 (4)	8.1 (4)

Table 2. *Selected geometric parameters* (Å, °)

N1—C2	1.398 (5)	S6—C9	1.740 (5)
N1—C5	1.411 (5)	C9—C10	1.375 (7)
N1—S6	1.680 (4)	C16—C17	1.387 (8)
C2—C3	1.358 (6)	C17—C18	1.373 (7)
C2—C19	1.490 (6)	C19—C20	1.494 (6)
C3—C4	1.431 (6)	C19—N23	1.255 (5)
C3—S24	1.762 (5)	C20—C21	1.532 (8)
C4—C5	1.383 (6)	C21—C22	1.453 (8)
C4—C15	1.401 (6)	C22—N23	1.474 (7)
C5—C18	1.394 (6)	S24—O25	1.474 (4)
S6—O7	1.422 (3)	S24—C26	1.799 (6)
S6—O8	1.417 (3)		
C2—N1—C5	107.7 (4)	O8—S6—C9	109.2 (2)
C2—N1—S6	124.7 (3)	S6—C9—C10	119.5 (4)
C5—N1—S6	126.8 (3)	S6—C9—C14	119.1 (4)
N1—C2—C3	108.9 (4)	C4—C15—C16	118.7 (5)
N1—C2—C19	125.4 (4)	C15—C16—C17	120.0 (5)
C3—C2—C19	125.6 (4)	C16—C17—C18	122.6 (5)
C2—C3—C4	108.1 (4)	C5—C18—C17	116.8 (5)
C2—C3—S24	122.4 (4)	C2—C19—C20	122.8 (4)
C4—C3—S24	129.2 (4)	C2—C19—N23	119.7 (4)
C3—C4—C5	107.4 (4)	C20—C19—N23	117.4 (4)
C3—C4—C15	132.5 (5)	C19—C20—C21	101.0 (5)
C5—C4—C15	120.1 (4)	C20—C21—C22	104.6 (5)
N1—C5—C4	107.8 (4)	C21—C22—N23	109.9 (5)
N1—C5—C18	130.5 (5)	C19—N23—C22	106.5 (4)
C4—C5—C18	121.6 (5)	C3—S24—O25	108.0 (2)
N1—S6—O7	105.4 (2)	C3—S24—C26	98.0 (2)
N1—S6—O8	106.1 (2)	O25—S24—C26	106.6 (3)
N1—S6—C9	105.2 (2)	S24—C26—C27	118.3 (5)
O7—S6—O8	120.7 (2)	S24—C26—C31	121.5 (5)
O7—S6—C9	109.0 (2)		

H atoms were placed in calculated positions (C—H = 0.95 Å) and given isotropic displacement factors 1.2 times the $B_{\rm eq}$ value of the atom to which they are bonded. Anomalous-dispersion effects were included in $F_{\rm calc}$ (Ibers & Hamilton, 1964).

The computer programs used were: *SHELXS*86 (Sheldrick, 1985), *DIRDIF* (Parthasarathi, Beurskens & Slot, 1983), *TEXSAN* (Molecular Structure Corporation, 1985) and *PLUTO* (Motherwell & Clegg, 1978).

We thank the SERC, UK, for funds for the purchase of the Rigaku AFC-5*R* diffractometer and for a studentship (JGK).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HU1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Bromo-12-phenyltetracene

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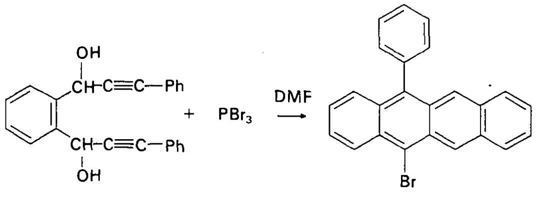
Abstract

X-ray structural analysis confirms that the title compound (5-bromo-12-phenylnapthacene, $C_{24}H_{15}Br$) consists of a tetracene ring system substituted in the 5 position by a Br atom and in the 12 position by a phenyl group. The tetracene portion of the compound is planar to within 0.05 Å, with the substituted phenyl group twisted out of the plane at angles of 108 and 102° for molecules *A* and *B*, respectively. The C—C bond lengths of the fused ring system are not identical, and are consistent with simple Pauling bond orders.

Comment

Although the crystal structures of tetracene, pentacene and hexacene (Robertson, Sinclair & Trotter, 1961; Campbell, Robertson & Trotter, 1961, 1962) were reported in the early sixties and an X-ray structural analysis was carried out on the monosubstituted compound 5-methyltetracene (Cox & Sim, 1979), no crystal structures of di-substituted tetracenes have been reported to date.

The title compound (I) was prepared by a modification of the literature method (Straub & Hambrecht, 1975) by treatment of a DMF solution of 1,2-bis(1-hydroxy-3-phenyl-2-propynyl)benzene with phosphorus tribromide at 273 K. The X-ray structural analysis described here confirmed that the product is 5-bromo-12-phenyltetracene. The molecular parameters of the two molecules in the asymmetric unit, *A* and *B*, are essentially the same and for the purpose of this work all bond lengths and angles are quoted as the mean of the respective values. The two molecules in the asymmetric unit are shown in Fig. 1.



(I)

The substituent phenyl ring bond distances in 5-bromo-12-phenyltetracene are consistent with π-electron delocalization and lie within the range 1.323 (11)–1.402 (13) Å. The phenyl group is twisted out of the plane of the tetracene backbone at angles of 108 and 102° for molecules *A* and *B*, respectively. This feature is probably a consequence of the

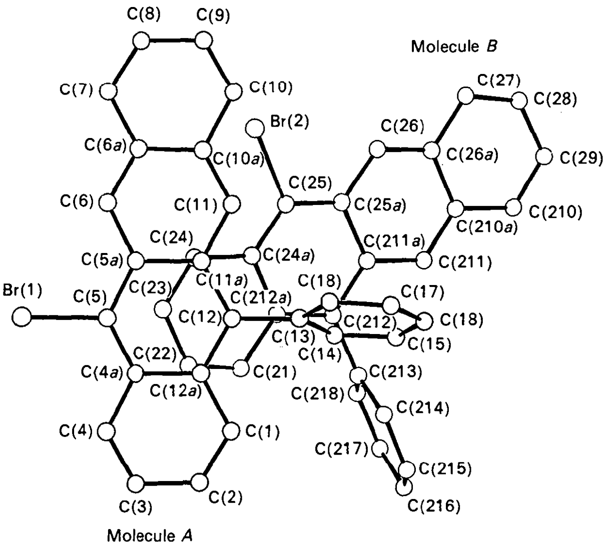


Fig. 1. The two independent molecules of 5-bromo-12-phenyltetracene in the asymmetric unit, drawn using *ORTEP*II (Johnson, 1976).

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