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1-(Phenylsulfonyl)-2-[1-(phenylsulfonyl)-2-(3,4,5-trimethoxyphenyl)ethyl]indole†

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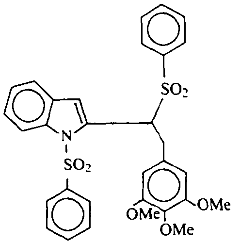
Abstract

The title compound contains an indole ring system with two phenylsulfonyl groups and one 3,4,5-trimethoxyphenyl group as exocyclic substituents. The methoxy groups in the 3,4,5-trimethoxyphenyl moiety are twisted with respect to the plane of the ring. One of the phenylsulfonyl ring systems and the ring of the 3,4,5-trimethoxyphenyl group are nearly perpendicular to the indole ring system, while the other phenylsulfonyl ring system is inclined at an angle of 30° to it.

Comment

The indole ring system is present in a number of natural products, many of which are found to possess psychotropic (Grinev, Trofimkin, Lomanova, Andreeva & Mashkovskii, 1978), antidepressant (Grinev *et al.*, 1984) and hypertensive (Merk, 1971) properties. They also exhibit antimicrobial (El-Sayed, Barnhart, Ammon & Wassel, 1986) and anti-inflammatory (Rodriguez, Temprano, Esteban-Calderon, Martinez-Ripoll & Garcia-Blanco, 1985) activity. Here we report the structure of the title compound, (I).



(I)

A perspective view (*PLUTO*; Motherwell & Clegg, 1976) of the molecule is shown in Fig. 1. The average S—O and S—C_{aryl} distances and the S—N distance of 1.427 (4), 1.779 (4) and 1.671 (2) Å, respectively, are comparable with those in most sulfonamides (Leger, Alberola & Carpy, 1977; Ghosh, Basak, Mazumdar & Sheldrick, 1989; Datta *et al.*, 1993), as are the distortions of the bond angles around the S atoms away from the ideal values for tetrahedral geometry. The largest deviations are in the O—S—O angles [O1—S1—O2 = 120.1 (2) and O3—S2—O4 = 119.1 (2)°]; the other O—S—*X* angles range from 106.4 (2) to 109.1 (2)°. The indole ring system is planar [$\Sigma(\Delta/\sigma)^2 = 28$], as observed in many natural-product derivatives (Cotrait & Barrans, 1974; Gartland, Freeman & Bugg, 1974; Vijayalakshmi & Srinivasan, 1975; Yamane, Andou & Ashida, 1977). The methoxy groups in the 3,4,5-trimethoxyphenyl ring at C3*b*, C4*b* and C5*b* are rotated from the plane of the phenyl ring [C2*b*—C3*b*—O5—C13 = −8.0 (9), C3*b*—C4*b*—O6—C14 = −94.5 (8) and C6*b*—C5*b*—O7—C12 = 12.5 (9)°]. The phenylsulfonyl ring *A*, bonded to the N atom of the indole moiety, is perpendicular to both the 3,4,5-trimethoxyphenyl ring *B* and the second phenylsulfonyl ring *C*; the interplanar angle between rings *A* and *B* is 84.0 (2)° and the angle between rings *A* and *C* is 86.6 (2)°. The plane through ring *A* makes an angle of 74.4 (2)° with the plane of the indole moiety. Ring *B* is inclined with respect to the indole moiety and ring *C* at angles of 85.2 (1) and 68.2 (1)°, respectively. The angle between ring *C* and the indole moiety is 30.1 (2)°. The packing of the molecules in the unit cell is purely due to van der Waals forces.

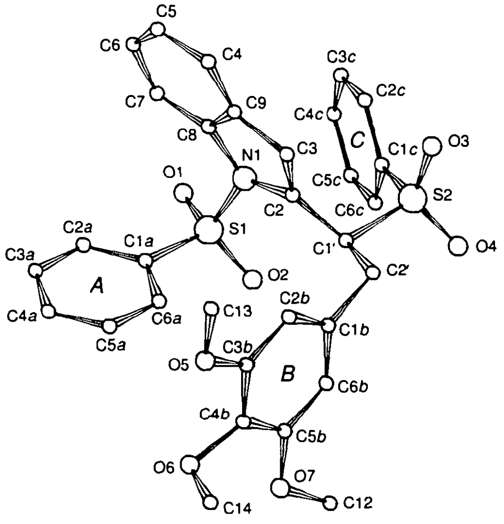


Fig. 1. A perspective view of the molecule with the atomic numbering scheme.

Experimental

The title compound was synthesized by means of a reductive condensation (Sadanandan, 1994). Good-quality crystals suitable for X-ray analysis were obtained from aqueous acetone.

Crystal data

$C_{31}H_{29}NO_7S_2$
$M_r = 591.69$
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å

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† DCB contribution No. 838.

Monoclinic
$P2_1/c$
$a = 11.844$ (2) Å
$b = 24.508$ (4) Å
$c = 11.021$ (3) Å
$\beta = 114.32$ (1)°
$V = 2915.2$ (11) Å^3
$Z = 4$
$D_x = 1.344$ Mg m^{-3}

Cell parameters from 20 reflections
$\theta = 20$–30°
$\mu = 2.02$ mm^{-1}
$T = 293$ K
Rectangular
0.37 × 0.32 × 0.21 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.67$, $T_{\max} = 0.94$
5111 measured reflections
4810 independent reflections
3418 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.017$
$\theta_{\max} = 70°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 29$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 100 reflections intensity variation: <2%

Refinement

Refinement on F
$R = 0.056$
$wR = 0.068$
$S = 1.82$
3418 reflections
478 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F) + 0.00685F^2]$
$(\Delta/\sigma)_{\max} = 0.051$
$\Delta\rho_{\max} = 0.534$ e Å^{-3}
$\Delta\rho_{\min} = -0.451$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

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

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

	x	y	z	$U_{\rm eq}$
N1	0.6322 (2)	0.6511 (1)	0.4044 (3)	0.0497 (1)
C2	0.6237 (3)	0.6038 (1)	0.4786 (3)	0.0473 (2)
C3	0.6119 (3)	0.5594 (1)	0.4027 (4)	0.0579 (2)
C4	0.6071 (4)	0.5462 (2)	0.1668 (4)	0.0747 (3)
C5	0.6113 (5)	0.5746 (2)	0.0614 (4)	0.0874 (3)
C6	0.6236 (4)	0.6303 (2)	0.0657 (4)	0.0809 (3)
C7	0.6328 (4)	0.6606 (2)	0.1745 (4)	0.0648 (2)
C8	0.6280 (3)	0.6321 (1)	0.2817 (3)	0.0500 (2)
C9	0.6156 (3)	0.5753 (1)	0.2791 (3)	0.0558 (2)
S1	0.7118 (1)	0.7078 (1)	0.4713 (1)	0.0629 (1)
O1	0.6612 (3)	0.7498 (1)	0.3743 (3)	0.0876 (2)
O2	0.7124 (3)	0.7137 (1)	0.5994 (3)	0.0727 (2)
C1*a*	0.8616 (4)	0.6933 (2)	0.4881 (4)	0.0715 (2)
C2*a*	0.9104 (5)	0.7193 (3)	0.4090 (5)	0.0779 (4)
C3*a*	1.0295 (7)	0.7065 (4)	0.4267 (8)	0.0889 (6)
C4*a*	1.0991 (5)	0.6698 (5)	0.5211 (8)	0.0915 (5)
C5*a*	1.0507 (5)	0.6445 (3)	0.5985 (7)	0.0928 (3)
C6*a*	0.9310 (4)	0.6562 (2)	0.5830 (6)	0.0884 (7)
C1′	0.6070 (3)	0.6067 (1)	0.6060 (3)	0.0533 (2)
S2	0.4422 (1)	0.6121 (1)	0.5702 (1)	0.0620 (1)
O3	0.3781 (2)	0.5662 (1)	0.4902 (3)	0.0800 (2)
O4	0.4352 (3)	0.6212 (1)	0.6951 (3)	0.0947 (2)
C1*c*	0.3905 (3)	0.6712 (1)	0.4734 (4)	0.0562 (2)
C2*c*	0.3278 (4)	0.6663 (2)	0.3357 (4)	0.0799 (3)
C3*c*	0.2864 (5)	0.7142 (3)	0.2624 (6)	0.0750 (4)
C4*c*	0.3107 (6)	0.7643 (3)	0.3259 (8)	0.0811 (5)
C5*c*	0.3711 (5)	0.7679 (2)	0.4578 (7)	0.0948 (4)
C6*c*	0.4123 (4)	0.7210 (2)	0.5350 (5)	0.0726 (3)
C2′	0.6560 (3)	0.5560 (2)	0.6955 (4)	0.0636 (2)
C1*b*	0.7962 (4)	0.5591 (2)	0.7667 (4)	0.0636 (2)
C2*b*	0.8692 (4)	0.5267 (2)	0.7268 (5)	0.0776 (3)
C3*b*	0.9966 (4)	0.5315 (3)	0.7881 (6)	0.0691 (4)
C4*b*	1.0508 (4)	0.5688 (3)	0.8915 (6)	0.0954 (4)
C5*b*	0.9765 (4)	0.5995 (3)	0.9351 (5)	0.0978 (4)
C6*b*	0.8496 (4)	0.5952 (2)	0.8712 (4)	0.0770 (3)
O5	1.0778 (4)	0.5016 (2)	0.7556 (2)	0.0813 (4)
O6	1.1807 (5)	0.5839 (3)	0.9357 (6)	0.0869 (5)
O7	1.0362 (4)	0.6337 (2)	1.0390 (5)	0.0691 (9)
C12	0.9637 (7)	0.6582 (3)	1.1001 (6)	0.0959 (4)
C13	1.0310 (7)	0.4588 (4)	0.6655 (9)	0.0880 (5)
C14	1.2314 (11)	0.5517 (4)	1.0297 (9)	0.0863 (7)

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

N1—C2	1.446 (4)	S2—O4	1.430 (4)
N1—C8	1.412 (5)	S2—C1*c*	1.753 (3)
N1—S1	1.671 (2)	C3*b*—O5	1.369 (9)
S1—O1	1.426 (3)	C4*b*—O6	1.457 (7)
S1—O2	1.416 (4)	C5*b*—O7	1.359 (7)
S1—C1*a*	1.743 (5)	O5—C13	1.393 (10)
C1′—S2	1.830 (4)	O6—C14	1.243 (11)
S2—O3	1.438 (2)	O7—C12	1.424 (10)
C8—N1—S1	119.2 (2)	S2—C1′—C2′	106.4 (3)
C2—N1—S1	125.1 (2)	C1′—S2—C1*c*	105.4 (1)
C2—N1—C8	107.1 (2)	C1′—S2—O4	106.4 (2)
N1—C2—C1′	124.0 (2)	C1′—S2—O3	108.8 (1)
N1—C2—C3	108.1 (3)	O4—S2—C1*c*	108.2 (1)
N1—C8—C7	130.5 (3)	O3—S2—C1*c*	108.0 (2)
N1—C8—C9	108.0 (3)	O3—S2—O4	119.1 (2)
N1—S1—C1*a*	104.0 (2)	S2—C1*c*—C2*c*	119.2 (3)
N1—S1—O2	107.1 (2)	C2*b*—C3*b*—O5	124.8 (5)
N1—S1—O1	106.4 (2)	C4*b*—C3*b*—O5	115.4 (5)
O2—S1—C1*a*	109.1 (2)	C3*b*—C4*b*—O6	120.5 (6)
O1—S1—C1*a*	108.8 (2)	C5*b*—C4*b*—O6	118.7 (6)
O1—S1—O2	120.1 (2)	C4*b*—C5*b*—O7	116.3 (5)
S1—C1*a*—C6*a*	118.6 (4)	C6*b*—C5*b*—O7	123.9 (5)
S1—C1*a*—C2*a*	120.7 (4)	C5*b*—O7—C12	116.9 (5)
C2—C1′—S2	110.0 (2)		

All H atoms were located from a ΔF map and were refined isotropically. Data collection, cell refinement and data reduction: *SDP* (Frenz, 1978). Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *SHELXS*76 (Sheldrick, 1976). Calculation of geometrical parameters: *PARST* (Nardelli, 1983). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances involving H atoms and least-squares-planes data have been deposited with the IUCr (Reference: VJ1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Macrobicyclic Thiophosphonamide Polyether Ligand

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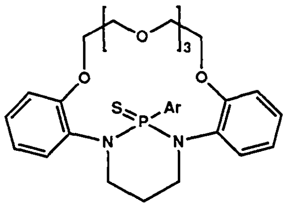
Abstract

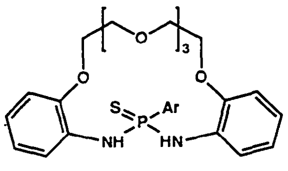
Two crystal structures of a macrobicyclic oligoether compound, 31-phenyl-8,11,14,17,20-pentoxa-1,27-diaza-31-phosphatetracyclo[25.3.1.$0^{2,7}$.$0^{21,26}$]henitriaconta-2,4,6,21,23,25-hexaene 31-sulfide, $C_{29}H_{35}N_2O_5PS$, (1), containing a thiophosphonamide group, are described. The molecules in the two crystals, (I) and (II), exhibit very similar conformations except for a disordered part in crystal form (II). A macrocyclic cavity appears in both conformations, although some O atoms of the $O(CH_2CH_2O)_4$ bridge are turned outwards. The propyl bridge and the phenyl group of the diazaphosphorinane moiety lie close to the sides of the macrocycle. The thiophosphoryl group is directed outwards.

Comment

The introduction of phosphorus binding sites in a host can markedly change its binding power and selectivity towards various guests. The title host, (1), is representative of a new class of organophosphorus ligands containing a crown macrocycle with phosphonamide groups as binding subunits (Dutasta, Declercq, Esteban-Calderon & Tinant, 1989; Dutasta, Van Oostenryck, Tinant & Declercq, 1993; Van Oostenryck, Tinant, Declercq, Dutasta & Simon, 1993). Compound (1) was designed to explore the feasibility and the properties of preorganized ligands based on our previously reported macrocyclic phosphorus host (2) (Dutasta & Simon, 1987). The introduction of the diazaphosphorinane ring enforces rigidity (Dutasta, Esteban-Calderon, Tinant & Declercq, 1990) and can afford two different configurations depending on the orientation of the substituents around the P atom. Therefore, we undertook the solid-state structure determination of compound (1), which was obtained by treatment of precursor (2) with propane diol ditosylate under basic conditions.



(1)



(2)

Two crystal forms of (1) exist and both are presented here. The first crystal form, (I), was obtained by evaporation from dichloromethane/hexane. The second, (II), appeared during unsuccessful attempts to complex potassium thiocyanate; it was obtained by evaporation from an acetone solution containing equimolar amounts of ligand (1) and potassium salt. As shown by the crystal structure analysis, no cation was included in this second crystal form.

The general folding of the molecule is very similar in the two structures. However, its must be noted that in the crystal form (II), disorder appeared involving four adjacent atoms of the polyether chain (C21–C24), with relative occupancies 0.72:0.28. This disorder implies two different conformations, which are reported in this discussion as (II*A*) and (II*B*). Fig. 1 is a view of structure (II*A*) giving the numbering of the atoms. In Fig. 2, the non-H atoms of (I) and (II*A*) are superimposed.

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