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Structural Investigations of 1,2,3,4-Tetrahydrocarbazole Derivatives. I. 2,3-Dihydro-9-(phenylsulfonyl)carbazole-4(1*H*)-one and 1,2,3,4-Tetrahydrocarbazole-1-spiro-2′-[1,3]dithiolane

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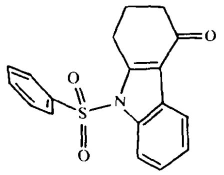
Abstract

Rings *A* and *B* of the title compounds, $C_{18}H_{15}NO_3S$ (1) and $C_{14}H_{15}NS_2$ (2), are planar while the hydrogenated *C* rings are not. The rings in the tetrahydrocarbazole skeleton are twisted with respect to each other.

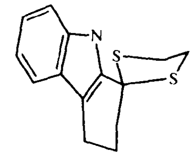
Comment

The title compounds have tricyclic ring systems with the rings named as *A*, *B* and *C* as in the strychnos type of indol alkaloids (Bosch & Bonjoch, 1988). Synthesis of these compounds is currently being studied using the title compounds as starting materials (Götz, Bats & Fritz, 1986; Patır & Fritz, 1990). When positions 2 or 3 of the title compounds were substituted by appropriate substituents, synthesis of the dasycarbidone skeleton was accomplished (Magnus, Sear, Kim & Vicker, 1992). The possibility of synthesizing the indol type of alkaloids by substitution at either position 1 or other positions is currently under investigation (Patır & Götz, 1993).

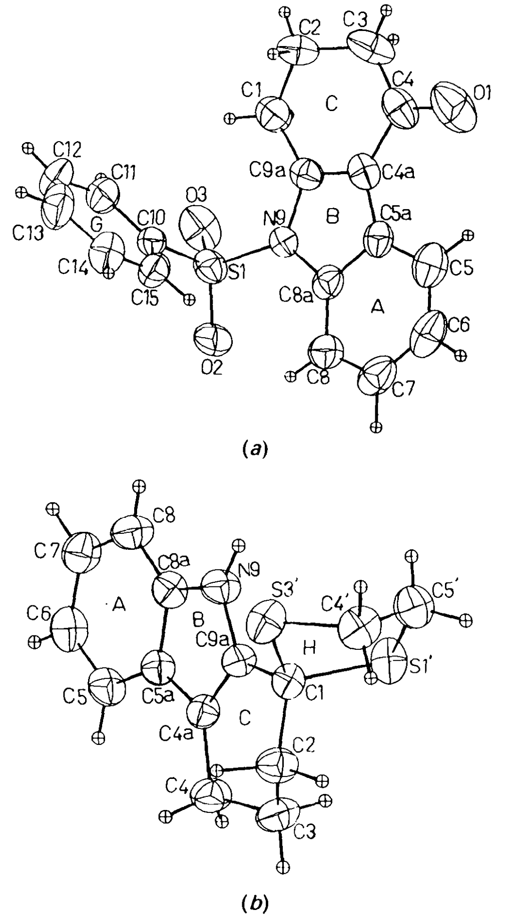
Compound (1) was prepared from tetrabutylammonium hydrogensulfate, benzoylsulfonyl chloride and 1,2,3,4-tetrahydrocarbazole-4-one by the method of Volker (1979) (see also Patır, 1991). Compound (2) was prepared from 1,2,3,4-tetrahydrocarbazole-1-one and ethanedithiol using $ZnCl_2$ as a catalyst (Patır & Götz, 1993). Perspective views of compounds (1) and (2) are shown in Fig. 1 and the crystal packings are presented in Fig. 2.



(1)



(2)



(*a*)

(*b*)

Fig. 1. *SNOOPI* (Davies, 1983) drawings of (*a*) compound (1) and (*b*) compound (2) with the atom-numbering schemes. The thermal ellipsoids are drawn at the 50% probability level.

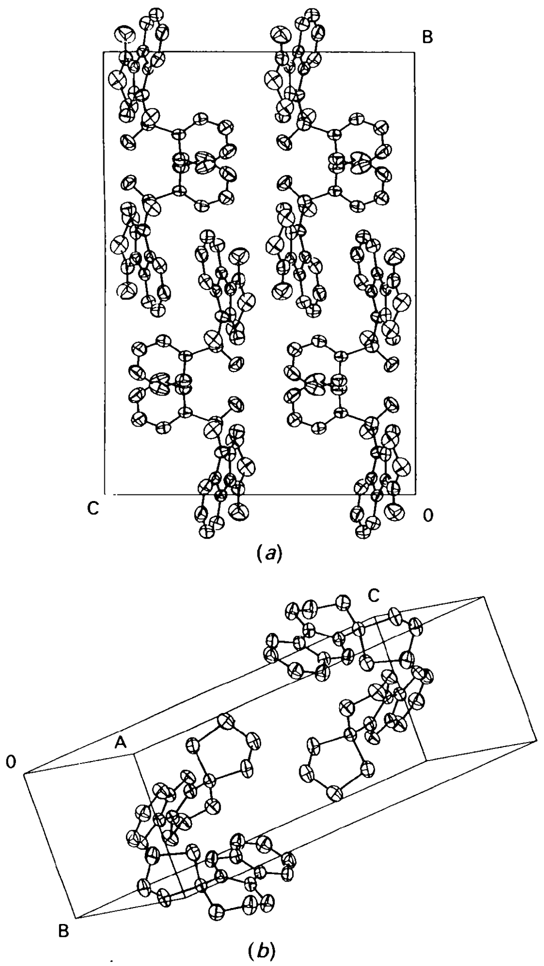


Fig. 2. Perspective views of the crystal packings of (*a*) compound (1) and (*b*) compound (2).

Generally, the back donation of the lone pair of electrons of the N9 atom affects the bond lengths within the *B* rings leading to small values for the carbazole skeleton. In compound (1), the electron-withdrawing character of the phenylsulfonyl group counteracts this affect causing larger bond lengths [C8a—N9 = 1.423 (5), C9a—N9 = 1.412 (5) Å] than in compound (2) [C8a—N9 = 1.392 (5), C9a—N9 = 1.372 (5) Å].

The sum of the angles about N9 is 359.2 (3)° in compound (1) and 359.9 (3)° in compound (2), so the atoms attached to it are planar. The corresponding bond angle values are given in Table 2.

Experimental

Compound (1)

Crystal data

$C_{18}H_{15}NO_3S$
$M_r = 325.38$
Orthorhombic
Pcab
$a = 8.952\ (5)$ Å
$b = 21.979\ (4)$ Å
$c = 15.709\ (3)$ Å
$V = 3090.8\ (1.9)$ Å^3
$Z = 8$
$D_x = 1.398$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5\text{-}12°$
$\mu = 0.21$ mm^{-1}
$T = 293$ K
Prismatic
1.1 × 0.45 × 0.35 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6408 measured reflections
2417 independent reflections
1389 observed reflections [$F \geq 3\sigma(F)$]

$\theta_{max} = 37.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 17$
3 standard reflections frequency: 180 min intensity variation: 1%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.032$
1210 reflections
268 parameters
All H-atom parameters refined

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

$C_{14}H_{15}NS_2$
$M_r = 261.4$
Monoclinic
$P2_1/c$
$a = 9.715\ (2)$ Å
$b = 6.721\ (2)$ Å
$c = 19.854\ (8)$ Å
$\beta = 91.29\ (3)°$
$V = 1296.0\ (7)$ Å^3
$Z = 4$
$D_x = 1.340$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 6\text{-}14°$
$\mu = 3.46$ mm^{-1}
$T = 293$ K
Plate
0.52 × 0.32 × 0.06 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical $T_{min} = 0.341$, $T_{max} = 0.855$
3986 measured reflections
2486 independent reflections

1847 observed reflections [$F \geq 3\sigma(F)$]
$\theta_{max} = 75°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 24$
3 standard reflections frequency: 180 min intensity variation: 1%

Refinement

Refinement on F
$R = 0.054$
$wR = 0.067$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.04$ e Å^{-3}
$\Delta\rho_{min} = -0.64$ e Å^{-3}

1616 reflections
214 parameters
All H-atom parameters refined

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

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

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

	x	y	z	U_{eq}
Compound (1)				
C1	−0.1568 (5)	0.3557 (2)	0.5748 (4)	0.0563 (17)
C2	−0.3182 (6)	0.3755 (3)	0.5825 (4)	0.069 (2)
C3	−0.3507 (6)	0.4359 (3)	0.5452 (4)	0.074 (3)
C4	−0.2457 (6)	0.4851 (2)	0.5717 (3)	0.0560 (18)
C4a	−0.0964 (5)	0.4660 (2)	0.5972 (3)	0.0437 (16)
C5	0.0489 (6)	0.5641 (2)	0.6387 (3)	0.063 (2)
C5a	0.0297 (5)	0.5015 (2)	0.6255 (2)	0.0440 (15)
C6	0.1840 (8)	0.5839 (2)	0.6703 (3)	0.070 (3)
C7	0.2991 (7)	0.5439 (3)	0.6892 (3)	0.067 (2)
C8	0.2845 (5)	0.4818 (3)	0.6753 (3)	0.0573 (19)
C8a	0.1467 (4)	0.4618 (2)	0.6436 (3)	0.0433 (14)
C9a	−0.0561 (4)	0.4067 (2)	0.5974 (2)	0.0437 (16)
C10	0.1137 (4)	0.3132 (2)	0.7409 (3)	0.0400 (14)
C11	0.0378 (6)	0.2592 (2)	0.7472 (4)	0.0577 (19)
C12	−0.0122 (6)	0.2406 (3)	0.8253 (4)	0.077 (3)
C13	0.0124 (6)	0.2750 (2)	0.8976 (4)	0.0720 (19)
C14	0.0891 (6)	0.3291 (2)	0.8905 (3)	0.0630 (18)
C15	0.1387 (5)	0.3484 (2)	0.8119 (3)	0.0500 (17)
N9	0.0945 (3)	0.4024 (1)	0.6233 (2)	0.0433 (12)
S1	0.1845 (1)	0.3369 (5)	0.6424 (8)	0.0480 (4)
O1	−0.2800 (4)	0.5392 (2)	0.5694 (3)	0.0953 (15)
O2	0.3386 (3)	0.3526 (1)	0.6515 (2)	0.0650 (12)
O3	0.1393 (4)	0.2951 (1)	0.5781 (2)	0.0680 (11)
Compound (2)				
C1	0.7991 (4)	0.0024 (6)	0.1070 (2)	0.0360 (11)
C2	0.8912 (5)	0.1836 (7)	0.0955 (2)	0.0493 (16)
C3	0.9962 (5)	0.2135 (9)	0.1528 (2)	0.0532 (16)
C4	0.9235 (5)	0.2634 (8)	0.2184 (2)	0.0494 (14)
C4′	0.7397 (5)	−0.1263 (8)	−0.0179 (2)	0.0530 (17)
C4a	0.8049 (4)	0.1258 (6)	0.2278 (2)	0.0367 (12)
C5	0.7228 (5)	0.1755 (7)	0.3513 (2)	0.0455 (11)
C5′	0.8045 (6)	−0.3086 (8)	0.0137 (2)	0.0543 (15)
C5a	0.7228 (4)	0.0924 (6)	0.2861 (2)	0.0378 (11)
C6	0.6236 (5)	0.1151 (8)	0.3952 (2)	0.0493 (16)
C7	0.5254 (5)	−0.0265 (7)	0.3769 (2)	0.0512 (17)
C8	0.5240 (5)	−0.1118 (8)	0.3137 (2)	0.0500 (14)
C8a	0.6229 (4)	−0.0509 (6)	0.2689 (2)	0.0397 (12)
N9	0.6431 (4)	−0.1031 (6)	0.2020 (2)	0.0437 (11)
C9a	0.7506 (4)	0.0066 (6)	0.1781 (2)	0.0363 (11)
S1′	0.8933 (1)	−0.2342 (2)	0.0907 (5)	0.0517 (4)
S3′	0.6512 (1)	0.0032 (2)	0.0481 (5)	0.0495 (4)

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

	(1)	(2)
C1—C2	1.513 (7)	1.531 (6)
C1—C9a	1.482 (6)	1.499 (5)
C1—S1′		1.867 (4)
C1—S3′		1.832 (4)
C2—C3	1.481 (7)	1.524 (6)
C3—C4	1.492 (7)	1.532 (7)
C4—C4a	1.457 (6)	1.492 (6)
C4—O1	1.229 (5)	
C4a—C5a	1.442 (6)	1.438 (5)
C4a—C9a	1.352 (5)	1.367 (5)
C5a—C5	1.402 (6)	1.409 (5)
C5a—C8a	1.391 (5)	1.404 (6)
C5—C6	1.378 (7)	1.377 (6)
C6—C7	1.386 (7)	1.390 (7)
C7—C8	1.389 (6)	1.379 (6)
C8—C8a	1.401 (6)	1.386 (6)
C8a—N9	1.423 (5)	1.392 (5)
C9a—N9	1.412 (5)	1.372 (5)
C5′—C4′		1.508 (7)
N9—S1	1.678 (3)	
C5′—S1′		1.808 (5)
C4′—S3′		1.807 (5)
N9—H9		0.85 (5)
C2—C1—C9a	110.1 (4)	108.8 (3)
C2—C1—S1′		111.2 (3)
C9a—C1—S1′		110.2 (3)
C9a—C1—S3′		110.0 (2)
S1′—C1—S3′		105.8 (2)
C2—C1—S3′		110.8 (3)
C1—C2—C3	114.4 (5)	112.1 (4)
C2—C3—C4	114.6 (5)	110.5 (4)
C3—C4—C4a	116.5 (4)	110.1 (4)
C3—C4—O1	122.4 (5)	
O1—C4—C4a	121.0 (5)	
C4—C4a—C5a	130.4 (4)	129.9 (4)
C4—C4a—C9a	121.5 (4)	124.0 (4)
C5a—C4a—C9a	108.1 (4)	106.1 (3)
C4a—C5a—C5	132.2 (4)	133.6 (4)
C4a—C5a—C8a	108.3 (3)	107.7 (3)
C8a—C5a—C5	119.5 (4)	118.7 (4)
C8a—N9—C9a	108.4 (3)	108.6 (3)
C8—C8a—N9	131.0 (4)	130.8 (4)
C5a—C8a—N9	106.4 (3)	107.1 (3)
C1—C9a—C4a	124.5 (4)	124.5 (3)
C1—C9a—N9	126.8 (4)	125.0 (3)
C4a—C9a—N9	108.7 (4)	110.5 (3)
C5′—C4′—S3′		106.9 (3)
C4′—C5′—S1′		108.3 (4)
C8a—N9—H9		123.5 (3)
C9a—N9—H9		127.8 (3)
C8a—N9—S1	126.2 (3)	
C9a—N9—S1	124.6 (3)	
C5′—S1′—C1		99.0 (2)
C1—S3′—C4′		94.7 (2)
C5a—C5—C6	118.1 (5)	118.7 (4)
C5—C6—C7	122.0 (5)	121.4 (4)
C6—C7—C8	121.2 (5)	121.4 (4)
C7—C8—C8a	116.5 (5)	117.9 (4)
C8—C8a—C5a	122.6 (4)	122.1 (4)
S1′—C1—C9a—C4a		108.5 (5)
S3′—C1—C2—C3		167.2 (4)
C1—C9a—C4a—C5a	178.0 (4)	176.2 (4)
C4—C4a—C9a—N9	178.9 (4)	179.8 (4)
C4a—C5a—C8a—C8	−177.9 (5)	−177.9 (4)
N9—C8a—C5a—C5	−179.5 (4)	178.2 (4)
O1—C4—C3—C2	−156.9 (4)	

H atoms were located by difference syntheses and refined isotropically. Initially, a unit-weighting scheme was used, but in the final stages of refinement the weights were assigned using the method described by Carruthers & Watkin (1979), as incorporated in the *CRYSTALS* package (Watkin, Carruthers & Betteridge, 1985). Other programs used were *SHELXS*86 (Sheldrick, 1990) and *SNOOPI* (Davies, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry including H-atom geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71515 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1076]

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Acta Cryst. (1994). C**50**, 453–456

2-(2,6-Di-*tert*-butylphenoxy)-2′,4,4,4′,4′,6,6,6′,6′-nonachloro-2,2′-bi(cyclotri-λ^5-phosphazene)

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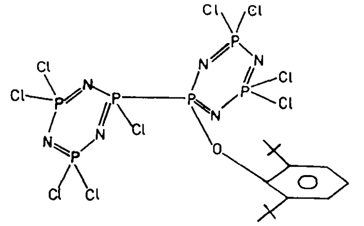
Abstract

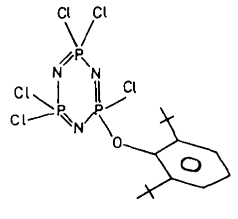
The title compound consists of the bulky 2,6-di-*tert*-butylphenoxy group and two phosphazene rings joined by a P—P bond [2.193 (2) Å]. The bulky group plays a predominant role in the distortion of the molecule as a whole. This distortion results in deviations of the benzene and phosphazene rings from planarity and twists the rings with respect to each other. In monocyclophosphazenes, the endocyclic angles about the P atom decrease while the exocyclic angles increase. This is in contrast to the behaviour of the title compound (a bicyclophosphazene) in which the exo- and endocyclic angles about the P atoms both decrease on substitution.

Comment

During the last two decades, the structure and properties of halophosphazenes have prompted an interest in the synthesis of new small-molecule organocyclophosphazenes and new inorganic backbone macromolecules (Allcock, Mang, McDonnel & Parvez, 1987). The organophosphazene derivatives are used in polymer synthesis and the resulting polymers are expected to have unique physical properties (Allcock, 1972; Allcock *et al.*, 1987). Polyphosphazenes with aryloxy, alkoxy and metallocenyl side groups are of special interest (Allcock, Riding & Whittle, 1984; Allcock *et al.*, 1987; Allcock, Manners, Mang & Parvez, 1990). We have investigated the reaction of sodium 2,6-di-*tert*-butylphenoxide and hexachlorocyclotriphosphazene, $N_3P_3Cl_6$. It is a highly complex reaction and yields at least two different products, a bicyclophosphazene derivative (I) and a monocyclophosphazene derivative (II).



(I)



(II)

During the reaction, the Cl atoms of compounds (I) and (II) can be substituted with 2,6-di-*tert*-butylphenoxy groups and the structural isomers (geminal, *cis–trans*) are probably formed. In this study, 2,6-di-*tert*-butylphenoxide was prepared from the reaction of 2,6-di-*tert*-butylphenol with metallic sodium (Çetinkaya, Gümrükçü & Lappert, 1980). The title compound (I), a bicyclophosphazene, was then synthesized by the reaction of hexachlorocyclotriphosphazene with the prepared sodium 2,6-di-*tert*-butylphenoxide and separated from the reaction mixture by column chromatography.

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