1368 reflections
188 parameters
H atoms: see below
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{\max} = <0.01$
$\Delta\rho_{\max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.23$ e Å$^{-3}$

Scattering factors from Stewart, Davidson & Simpson (1965) (H atoms) and Cromer & Waber (1974) (C and O atoms)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—C15 | 1.505 (4) | C8—C16 | 1.498 (4) |
| O1—C15 | 1.425 (4) | O2—C16 | 1.438 (4) |
| C2—C1—C15 | 121.8 (3) | C7—C8—C16 | 119.4 (3) |
| C13—C1—C15 | 119.5 (3) | C12—C8—C16 | 120.9 (3) |
| O1—C15—C1 | 113.3 (3) | O2—C16—C8 | 110.3 (3) |
| C15—O1—H1O1 | 106 (2) | C16—O2—H1O2 | 106 (2) |

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1O1···O2$^{i}$ | 0.92 (5) | 1.80 (5) | 2.710 (3) | 168 (4) |
| O2—H1O2···O1$^{ii}$ | 0.88 (4) | 1.85 (4) | 2.715 (3) | 168 (3) |

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

The scan widths used were $(1.50 + 0.35\tan\theta)^\circ$ in $\omega$, with a background to scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry-indicated space group $P2_1/n$ (No. 14) and since refinement proceeded well it was adopted. Fourier difference methods were used to locate the H-atom positions. In later stages of refinement, the ring H atoms H2–H7, H9 and H10 were made canonical, with a C—H distance of 0.98 Å and $U_{\rm iso}$ values $1.2U_{\rm eq}$ of the associated C atom. All the H atoms of the two hydroxymethyl groups were refined isotropically. The maximum effect of extinction was 1.2% of $F_o$ for 014. The maximum positive residual peak was located near the midpoint of the C9—C12 bond and the maximum negative peak was located near the center of the C1–C4/C13–C14 ring. A second crystal was oriented on the diffractometer to demonstrate that the *b* axis is oriented along the long column axis of these crystals. It is noted that the proportion of observed reflections is rather low (~44%), the reason for this not being known.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1309). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*Acta Cryst.* (1997). C**53**, 771–773

# 4-Hydroxy-6-methoxy-9-phenylsulfonylcarbazol-3-yl Methyl Ketone

L. GOVINDASAMY,[a] D. VELMURUGAN,[a] K. RAVIKUMAR[b] AND A. K. MOHANAKRISHNAN[c]

[a]*Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India,* [b]*Laboratory of Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India, and* [c]*Department of Organic Chemistry, University of Madras, Guindy Campus, Madras 600 025, India. E-mail: crystal@giasmd01.vsnl.net.in*

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## Abstract

The asymmetric unit of the crystals of the title compound, $C_{21}H_{17}NO_5S$, contains two crystallographically independent molecules, each consisting of a carbazole

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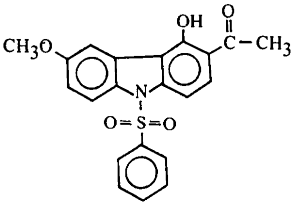
moiety and a phenylsulfonyl group. The geometry around the S atoms is distorted from that of a regular tetrahedron.

## Comment

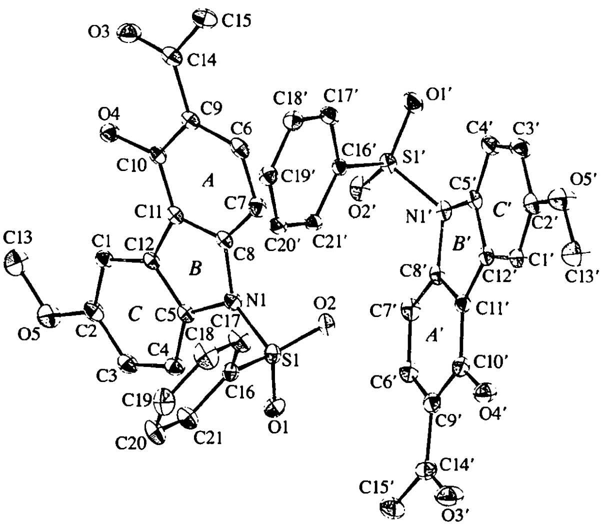
Carbazole alkaloids are well known DNA intercalating agents (Jain, Bhandary & Sobell, 1979). Carbazole compounds have pronounced biological activity due to the presence of oxygenated substituents (Hewlins, Oliveira-Campos & Shannon, 1984). A carbazole antibiotic, carbazomycin B, has pronounced antibacterial and antiyeast activity and inhibits the growth of some phytopathogenic fungi (Knolker & Bauermeister, 1989). A number of carbazole derivatives are being used in clinical trials against several human tumors (Gribble, 1990). The crystal structure analysis of the title compound, (I), was undertaken to ascertain the conformation of the phenylsulfonyl group with respect to the carbazole moiety.



(I)

The fused-ring system in both molecules is planar, with average deviations of 0.015 and 0.019 Å for molecules *A* and *B*, respectively. This planarity is thought to be essential for intercalation with DNA (Neidle, 1979). The carbazole moieties are inclined to the phenylsulfonyl group at 92.1 (3) and 67.4 (3)° for molecules *A* and *B*, respectively.

The angular disposition of the bonds about the S atoms in both the molecules deviates significantly from that of a regular tetrahedron, with the largest deviation in the O—S—O angle. The widening of the O—S—O angle (120.2 for molecule *A* and 119.3° for molecule *B*) from the ideal tetrahedral value is presumably the result of the repulsive interactions between the short S═O bonds. In both molecules, the electron-withdrawing character of the phenylsulfonyl group affects C—N bond lengths [N1—C8 1.430 (3), N1—C5 1.447 (4), N1′—C8′ 1.426 (3), N1′—C5′ and 1.455 (3) Å]. The sums of the angles about N1 and N1′ are 356.5 (2) and 345.5 (2)°, respectively. These angles are smaller than those found in 2,3-dihydro-9-phenylsulfonylcarbazole (Hökelek, Patir, Gülce & Okay, 1994). The exocyclic angles around C2 and C2′ in both molecules are markedly asymmetric (the C1—C2—O5 angle is about 9° larger than that of C3—C2—O5 in molecule *A* and the C1′—C2′—O5′ angle is 8.2° larger than that of C3′—C2′—O5′ in molecule *B*). The packing of molecules is stabilized by C—H···O and O—H···O hydrogen bonds.



Molecule *A* Molecule *B*

Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

## Experimental

The title compound was synthesized by the reductive condensation process (Mohanakrishnan & Srinivasan, 1993). Good quality crystals were obtained using methanol as solvent.

### *Crystal data*

$C_{21}H_{17}NO_5S$
$M_r = 395.42$
Monoclinic
$P2_1/c$
$a = 12.868\ (1)$ Å
$b = 14.951\ (1)$ Å
$c = 20.436\ (1)$ Å
$\beta = 105.58\ (1)°$
$V = 3787.2\ (4)$ Å$^3$
$Z = 8$
$D_x = 1.387$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7–17°$
$\mu = 0.204$ mm$^{-1}$
$T = 293\ (2)$ K
Cube
0.35 × 0.25 × 0.20 mm
Light yellow

### *Data collection*

Siemens *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5238 measured reflections
4980 independent reflections
3504 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0401$
$\theta_{\rm max} = 23°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = -22 \rightarrow 21$
2 standard reflections every 200 reflections intensity decay: <1%

*Refinement*

Refinement on $F^2$
$R(F) = 0.0457$
$wR(F^2) = 0.1332$
$S = 1.071$
4980 reflections
633 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.4343P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.078$
$\Delta\rho_{\max} = 0.233$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.208$ e Å$^{-3}$
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0015 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| S1—O2 | 1.428 (2) | S1′—O2′ | 1.423 (2) |
| S1—O1 | 1.429 (2) | S1′—O1′ | 1.430 (2) |
| S1—N1 | 1.670 (2) | S1′—N1′ | 1.684 (2) |
| S1—C16 | 1.751 (3) | S1′—C16′ | 1.756 (3) |
| N1—C8 | 1.430 (3) | N1′—C8′ | 1.426 (3) |
| N1—C5 | 1.447 (3) | N1′—C5′ | 1.455 (3) |
| O2—S1—O1 | 120.19 (12) | O2′—S1′—O1′ | 119.33 (12) |
| O2—S1—N1 | 106.45 (11) | O2′—S1′—N1′ | 107.01 (12) |
| O1—S1—N1 | 106.03 (11) | O1′—S1′—N1′ | 107.18 (11) |
| O2—S1—C16 | 108.58 (13) | O2′—S1′—C16′ | 108.86 (12) |
| O1—S1—C16 | 108.81 (12) | O1′—S1′—C16′ | 110.07 (12) |
| N1—S1—C16 | 105.87 (12) | N1′—S1′—C16′ | 103.11 (11) |
| C8—N1—C5 | 106.8 (2) | C8′—N1′—C5′ | 106.1 (2) |
| C8—N1—S1 | 123.7 (2) | C8′—N1′—S1′ | 121.0 (2) |
| C5—N1—S1 | 126.0 (2) | C5′—N1′—S1′ | 118.4 (2) |

Data collection: *P*3 *Software* (Siemens, 1991). Cell refinement: *P*3 *Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*92 (Vickovic, 1994). Software used to prepare material for publication: *SHELXL*93 and *PARST*95 (Nardelli, 1983).

The authors thank Professor P. C. Srinivasan for providing the compound.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: VJ1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# A Tricyclic Phosphorus(V)–Hydrazine System with Twist Conformation of the Central Heterocycle

UDO ENGELHARDT AND MEHDI ROSEFID

*Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany. E-mail: udoengel@blume.chemie.fu-berlin.de*

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## Abstract

The compound 9-oxo-2-phenoxy-1,3,8,10-tetraaza-$2\lambda^5$-phosphatricyclo[8.4.0.0$^{3,8}$]tetradecane 2-sulfide, $C_{15}H_{21}N_4O_2PS$, was synthesized from bis(hexahydropyridazido)thiophosphoric acid *O*-phenyl ester and bis(trichloromethyl)carbonate trisphosgene in the presence of triethylamine. The molecular structure of the tricyclic system consists of a central six-membered ring with a twist conformation, the two anellated hexahydropyridazine rings revealing 'normal' chair conformations. Bond distances are N—N 1.429 (3) and 1.420 (3), P—N 1.647 (2) and 1.663 (2), and P—S 1.913 (1) Å.

## Comment

Inorganic six-membered rings containing phosphorus(V) and two hydrazine fragments as building blocks reveal, in many cases, an unusual twist conformation. The 'normal' chair conformation is destabilized by short N—N bond lengths, substituents at the four N atoms and large heteroatoms in the ring (Engelhardt, Bünger & Viertel, 1984; Engelhardt & Stromburg, 1985, 1987, 1992, 1993; Engelhardt & Giersdorf, 1986; Engelhardt & Simon, 1992*a*,*b*, 1993; Engelhardt, Stromburg & Simon, 1994; Engelhardt & Rosefid, 1994; Diefenbach, Stromburg & Engelhardt, 1995). In fused saturated ring systems, there are examples of the central $P^V$–hydrazine heterocycle having a chair conformation or a twist conformation depending on the configuration at the $P^V$ atoms in opposite positions of the ring: a *cis* configuration of the large S-atom substituents at the two P atoms in these positions leads to a twist conformation, whereas a *trans* configuration of these substituents gives a normal chair form of the

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