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Ethyl 4,6-Dimethoxy-9-phenylsulfonylcarbazole-3-carboxylate†

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Abstract

The crystal structure of the title compound, $C_{23}H_{21}NO_6S$, has been determined. The planar carbazole ring subtends an angle of 82.7 (4)° with the phenylsulfonyl group. The lengthening or shortening of the C—N bond distances [C5—N = 1.437 (4), C6—N = 1.418 (4) Å] is due to the electronic withdrawing character of the phenylsulfonyl group. The S atom is in the usual distorted tetrahedral configuration.

Comment

Tetrahydrocarbazoles are important synthons for the synthesis of alkaloids (Gramain, Husson & Troin, 1985). Their structures are analogous to that of ellipticine (Courseille, Busetta & Hospital, 1974), a plant alkaloid having pronounced anti-tumour activity (Kansal & Potier, 1986). These types of carbazole derivatives are used as starting materials in the synthesis of carbazole alkaloid (8*H*-quino[4,3-*b*]carbazole), which may be used to intercalate with DNA (Mohanakrishnan & Srinivasan, 1995). Owing to the planar chromophore of the carbazoles the pharmacological activity is based, first of all, on complex formation with human B-DNA (Gribble, 1990). The carbazole antibiotics carbazomycins A and B inhibit the growth of phytopathagenic fungi and have weak anti-bacterial and anti-yeast activities (Knolker & Bauermeister, 1989). Apart from the above biological importance these derivatives are used as photoconductors and also play a crucial role in determining the chain-growth directions in the solid-state polymerization. The crystal structure analysis of this compound was undertaken to ascertain the conformation of the phenylsulfonyl group with respect to the carbazole moiety of the molecule.

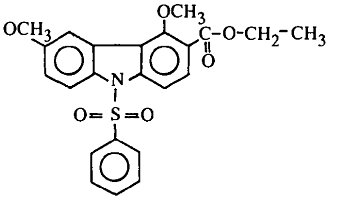

Fig. 1 shows an *ORTEP* (Johnson, 1976) diagram of the molecule with the atomic numbering scheme. The S atom exhibits the usual distorted tetrahedral configuration with the larger deviations in the O—S—O angles [O1—S—O2 = 119.83 (13)°] and the O1—S—N and O2—S—N angles [106.87 (13) and 106.60 (12)°, respectively]. The higher values of the C—N distances [C5—N = 1.437 (4), C6—N = 1.418 (4) Å] are caused by the electronic withdrawing character of the phenylsulfonyl group and this observation is in agreement with a related structure (Rodriguez, del Valle, Calderon & Ripoll, 1995). The S—N bond distance [1.660 (2) Å] lies in the range 1.63–1.69 Å (Cotton & Stokely, 1970). The S—O1 [1.425 (2) Å] and S—O2 [1.423 (2) Å] bonds are almost equal in distance to those of 1.430 (6) and 1.441 (6) Å, respectively, in 4-amino-*N*-(2-pyrimidinyl)-benzene sulfonamide (Kokila, Puttaraja, Kulkarni & Thampi, 1995). The conformation of the molecule can be described by the different torsion angles around the C18—S and S—N bonds. The torsion angles N—S—C18—C19 and N—S—C18—C23 are 66.9 (3) and −115.4 (2)°, respectively, and lie within the range $|\varepsilon_2|$ = 70–120° (Gomes *et al.*, 1993). The C18—S—N—C5 torsion angle of 64.8 (2)° lies within the range $|\varepsilon_1|$ = 60–90° (Cotton & Stokely, 1970). The sum of the angles about N, 354.8 (2)°, is shorter than the sum

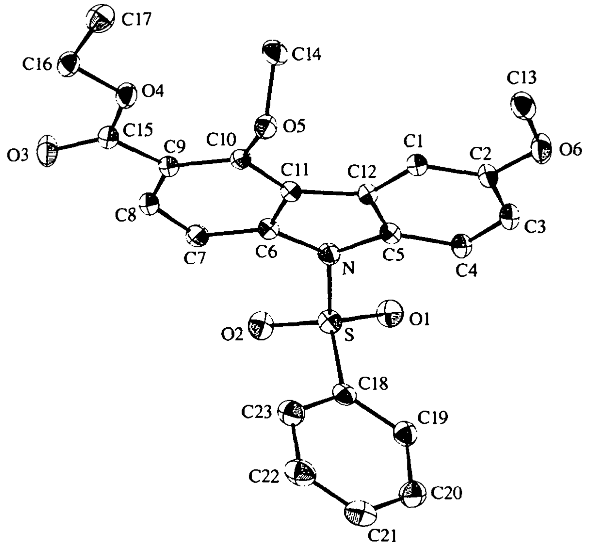

Fig. 1. Structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

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† DCB contribution No. 879.

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of the angles about N found in 2,3-dihydro-9-(phenylsulfonyl)carbazole, 359.2 (3)° (Hokelek, Patir, Gulce & Okay, 1994), so the atoms attached to it are planar. The planar carbazole ring fragment is inclined at an angle of 82.7 (4)° to the phenylsulfonyl group. The dispositions of the two sulfonyl O atoms O1 and O2 with respect to the phenyl ring are found to be somewhat asymmetrical, as indicated by the torsion angles O2—S—C18—C19 −46.8 (3), O2—S—C18—C23 130.9 (2), O1—S—C18—C19 −179.1 (2), O1—S—C18—C23 −1.4 (3)°. Atom O6 almost lies in the plane of the carbazole moiety and the deviation observed is only 0.0867 (2) Å.

The exocyclic angles around C2 and C10 are markedly asymmetric, O6—C2—C3 being 9.3 (3)° smaller than O6—C2—C1, and O5—C10—C11 being 5.8 (2)° smaller than O5—C10—C9. The dihedral angles of the dimethoxy group are C13—O6—C2—C1 = −0.7 (5) and C14—O5—C10—C9 = −87.9 (3)°.

Experimental

The title compound was synthesized by reductive condensation (Mohanakrishnan & Srinivasan, 1993). Crystals were grown from methanol at room temperature.

Crystal data

$C_{23}H_{21}NO_6S$
$M_r = 439.47$
Triclinic
$P\bar{1}$
$a = 7.9290 (10)$ Å
$b = 11.001 (2)$ Å
$c = 12.436 (2)$ Å
$\alpha = 75.540 (10)°$
$\beta = 83.540 (10)°$
$\gamma = 89.780 (10)°$
$V = 1043.4 (3)$ Å^3
$Z = 2$
$D_x = 1.399$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–$15°$
$\mu = 0.196$ mm^{-1}
$T = 293 (2)$ K
Rectangular
0.39 × 0.30 × 0.25 mm
Colourless

Data collection

Siemens $R3m/V$ diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2988 measured reflections
2748 independent reflections
2383 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0380$
$\theta_{\rm max} = 23°$
$h = -8 \rightarrow 0$
$k = -11 \rightarrow 11$
$l = -13 \rightarrow 13$
2 standard reflections every 60 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0383$
$wR(F^2) = 0.1280$
$S = 0.626$
2746 reflections
365 parameters

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.554$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.236$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1341P)^2 + 1.4912P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction coefficient: 0.004 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S—O2	1.423 (2)	O4—C15	1.322 (4)
S—O1	1.425 (2)	O4—C16	1.452 (4)
S—N	1.660 (2)	O5—C10	1.373 (3)
S—C18	1.760 (3)	O5—C14	1.429 (4)
N—C6	1.418 (4)	O6—C2	1.371 (4)
N—C5	1.437 (4)	O6—C13	1.418 (4)
O3—C15	1.207 (3)		
O2—S—O1	119.83 (13)	O6—C2—C3	114.8 (3)
O2—S—N	106.60 (12)	C4—C5—N	129.1 (3)
O1—S—N	106.87 (13)	C12—C5—N	108.7 (2)
O2—S—C18	108.90 (14)	C7—C6—N	130.0 (3)
O1—S—C18	108.96 (14)	C11—C6—N	108.6 (2)
N—S—C18	104.61 (12)	O5—C10—C11	117.4 (2)
C6—N—C5	107.4 (2)	O5—C10—C9	123.2 (2)
C6—N—S	124.8 (2)	O3—C15—O4	122.8 (3)
C5—N—S	122.6 (2)	O3—C15—C9	122.2 (3)
C15—O4—C16	115.8 (2)	O4—C15—C9	115.0 (2)
C10—O5—C14	115.3 (2)	O4—C16—C17	107.1 (3)
C2—O6—C13	118.0 (2)	C23—C18—S	119.9 (2)
O6—C2—C1	124.1 (3)	C19—C18—S	118.9 (2)
O2—S—N—C6	28.8 (3)	C14—O5—C10—C9	−87.9 (3)
O1—S—N—C6	158.1 (2)	O2—S—C18—C23	130.9 (2)
C18—S—N—C6	−86.5 (2)	O1—S—C18—C23	−1.4 (3)
O2—S—N—C5	−179.9 (2)	N—S—C18—C23	−115.4 (2)
O1—S—N—C5	−50.6 (2)	O2—S—C18—C19	−46.8 (3)
C18—S—N—C5	64.8 (2)	O1—S—C18—C19	−179.1 (2)
C13—O6—C2—C1	−0.7 (5)	N—S—C18—C19	66.9 (3)
S—N—C5—C4	23.8 (4)	S—C18—C19—C20	177.3 (3)
S—N—C5—C12	−157.6 (2)	S—C18—C23—C22	−175.9 (2)
S—N—C6—C7	−24.5 (4)		

Data collection: *R3m/V* diffractometer software. Cell refinement: *R3m/V* diffractometer 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 (Vicković, 1994). Software used to prepare material for publication: *SHELXL*93, *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1141). Services for accessing these data are described at the back of the journal.

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An Eight-Membered N,N,S,S-Heterocyclic Compound: 4,7-Bis(4-chlorophenyl)-3,8-dihydro-1,2,5,6-dithiadiazocine

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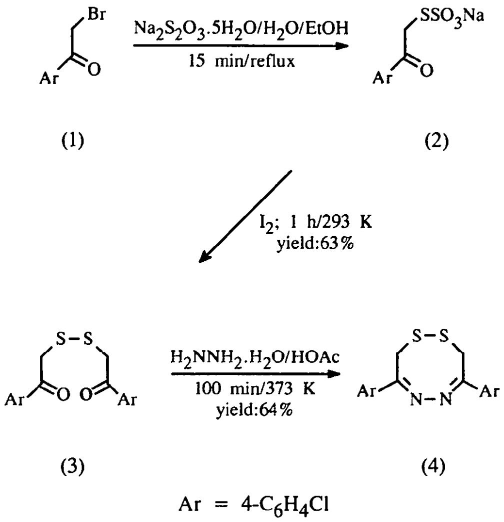
Abstract

The eight-membered ring in the title compound, $C_{16}H_{12}Cl_2N_2S_2$, adopts a non-planar conformation as expected, and the least-squares planes of the 4-substituted aromatic ring form a dihedral angle of 83.3 (2)° as a result of steric constraints. The molecular dimensions are of general interest for comparison with structural data of analogous compounds.

Comment

The experimental investigations were performed in order to develop efficient syntheses for substituted eight-membered heterocycles. The cyclization of 1,*n*-difunctional carbonyl compounds can be accomplished with hydrazine to give five- and six-membered N,N-heterocycles (Kost & Grandberg, 1966; Tišler & Stanovnik, 1968). In the same manner cyclization to form seven-membered N,N- and N,N,S-heterocycles (Lipp, Dallacker & Munnes, 1958; Sataty, 1970; Cuthbertson, Hardy & MacNicol, 1975) is also an effective synthetic route. The preparation of eight-membered N,N,S,S-heterocycles could be an interesting possibility.

With this in mind, 2-bromo-1-(4-chlorophenyl)ethan-1-one, (1), in ethanol was treated with sodium thiosulfate pentahydrate in water (reflux); the resulting Bunte salt, (2), (Distler, 1967) can be converted by treatment with iodine (Hiskey, Thomas & Kepler, 1964) to the corresponding bis(4-chlorophenacyl)disulfide, (3). The cyclizing condensation of this 1,6-difunctional intermediate can be achieved with hydrazine monohydrate in acetic acid and facilitates the efficient preparation of the target molecule, (4).



The constitution of the title compound can be deduced from ^1H and ^{13}C NMR ($CDCl_3$, 400 MHz) experiments. The *AB* signal (δ_A = 3.46, δ_B = 4.15 p.p.m.; J_{AB} = 12.8 Hz) is characteristic of the cyclic methylene groups being not equivalent. The Raman absorption for the S—S bond (ν = 512.9 cm^{-1}) is consistent with fundamental results (van Wart & Scheraga, 1976).

X-ray diffraction measurements were carried out to confirm these preliminary spectroscopic results and to determine the conformation of the target molecule in the solid phase.

The spectroscopic conclusions regarding the eight-membered ring are confirmed by the results of the X-ray analysis. The structure of the N,N,S,S-heterocycle is nearly regular, as demonstrated by the almost equivalent values for corresponding bond lengths S—C [1.835 (5), 1.829 (4) Å], C—C [1.510 (6), 1.496 (6) Å] and N—C [1.286 (6), 1.281 (5) Å].

The conformation of the eight-membered ring is determined by the spatial arrangement of the azine group. The electronic repulsion of the lone-pair electrons at the N atoms is reduced by distortion around the N—N bond; the value of 83.6 (5)° for the C—N—N—C torsion angle of the azine group is remarkable.

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