C12	0.0845 (2)	0.3235 (4)	0.1942 (2)	0.0290 (9)
C13	0.0626 (2)	0.4384 (4)	0.1275 (2)	0.0351 (10)
C14	−0.0512 (3)	0.4974 (5)	0.0852 (2)	0.0439 (12)
C15	−0.1447 (3)	0.4378 (5)	0.1085 (2)	0.0456 (11)
C16	−0.1248 (3)	0.3249 (5)	0.1750 (2)	0.0440 (11)
C17	−0.0108 (2)	0.2696 (4)	0.2182 (2)	0.0386 (10)

Table 2. *Geometric parameters* (Å, °)

O—C9	1.226 (4)	C8a—C9	1.483 (3)
C1—C2	1.372 (4)	C8a—C10a	1.408 (4)
C1—C9a	1.401 (3)	C9—C9a	1.482 (4)
C2—C3	1.379 (5)	C10—C10a	1.479 (4)
C3—C4	1.383 (4)	C10—C11	1.346 (4)
C4—C4a	1.400 (4)	C11—C12	1.483 (3)
C4a—C9a	1.398 (4)	C12—C13	1.385 (4)
C4a—C10	1.486 (3)	C12—C17	1.392 (4)
C5—C6	1.373 (5)	C13—C14	1.387 (4)
C5—C10a	1.400 (3)	C14—C15	1.377 (5)
C6—C7	1.385 (5)	C15—C16	1.376 (5)
C7—C8	1.376 (4)	C16—C17	1.385 (4)
C8—C8a	1.388 (4)		
C2—C1—C9a	120.8 (3)	C1—C9a—C9	118.7 (3)
C1—C2—C3	119.4 (2)	C4a—C9a—C9	121.1 (2)
C2—C3—C4	120.8 (3)	C10a—C10—C11	124.1 (2)
C3—C4—C4a	120.8 (3)	C10a—C10—C4a	115.9 (2)
C4—C4a—C9a	118.0 (2)	C4a—C10—C11	119.8 (2)
C4—C4a—C10	122.0 (3)	C5—C10a—C8a	117.7 (3)
C9a—C4a—C10	119.9 (2)	C5—C10a—C10	122.5 (3)
C6—C5—C10a	120.7 (3)	C8a—C10a—C10	119.7 (2)
C5—C6—C7	121.3 (3)	C12—C11—C10	130.3 (3)
C6—C7—C8	118.8 (3)	C13—C12—C17	118.2 (2)
C7—C8—C8a	121.1 (3)	C13—C12—C11	121.8 (3)
C8—C8a—C9	118.7 (3)	C17—C12—C11	119.8 (2)
C8—C8a—C10a	120.2 (2)	C14—C13—C12	121.1 (3)
C9—C8a—C10a	120.8 (2)	C15—C14—C13	119.7 (3)
C9a—C9—O	121.6 (2)	C16—C15—C14	120.1 (3)
C9a—C9—C8a	116.6 (2)	C17—C16—C15	120.1 (3)
O—C9—C8a	121.6 (3)	C12—C17—C16	120.7 (3)
C1—C9a—C4a	120.2 (3)		

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Structures of Pyrazole Derivatives. II. A Potential Bioisoster of Acetazolamide

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Abstract

In 5-Chloro-3-methyl-1-phenyl-4-pyrazolesulphonamide, the phenyl and pyrazole rings are planar making a dihedral angle of 54.4 (2)°. The molecular packing involves an intermolecular hydrogen bond: $N(3) \cdots N(2^i) = 2.951$ (8), $N(2^i) \cdots H'(N3) = 1.987$ (6) Å, $N(3)—H'(N3) \cdots N(2^i) = 154.8$ (4)° [symmetry operation: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$].

Comments

Among the sulfonamide derivatives commonly used as diuretics, one of the most important is acetazolamide (2) (de Stevens, 1963) which is commercially available in Brazil as DIAMOX (DEF, 1991). Because of the close bioisosteric relationship between the pyrazole and the 1,3,4-thiodiazole groups, and following a research program aimed at synthesizing potentially bioactive functionalized pyrazoles (Caracelli, Zukerman-Schpector, Barreiro & Freitas, 1992), compound (1) was prepared (Freitas, 1991). In order to determine its overall conformation a three-dimensional crystal structure determination was undertaken.
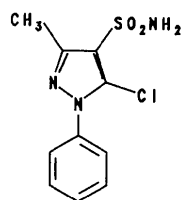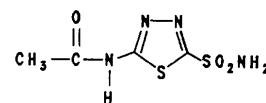
(1) (2)

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As can be seen in Table 2, the internal and external angles of the pyrazole ring follow the set of empirical rules given by Bonati & Bovio (1990), that is (a) N(1)—N(2)—C(3) is smaller than N(2)—N(1)—C(5); (b) N(2)—C(3)—C(4) is larger than N(1)—N(2)—C(3), C(3)—C(4)—C(5) and N(1)—C(5)—C(4); (c) C(3)—C(4)—C(5) is not the largest internal angle; (d) N(2)—N(1)—C(6) is smaller than C(5)—N(1)—C(6); (e) N(2)—C(3)—C(12) is smaller than C(4)—C(3)—C(12); and (f) S—C(4)—C(3) and S—C(4)—C(5) are equal.

The C(4)—C(5) distance is marginally shorter than C(3)—C(4) as expected in neutral pyrazole rings (Zukerman-Schpector, Castellano, Oliva, Massabni & Pinto, 1984, and references therein).

The pyrazole and phenyl rings are planar to within experimental accuracy, σ_{av} [defined as $(\Sigma_i d_i^2/N - 3)^{1/2}$] being 0.002 and 0.018 Å, respectively.
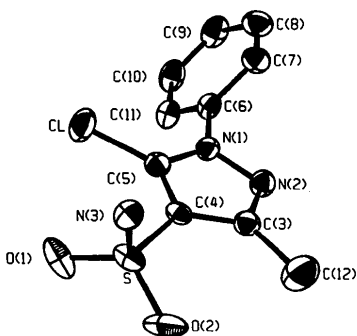

Fig. 1. Structure of (1).

Experimental

Crystal data

$C_{10}H_{10}ClN_3O_2S$
$M_r = 271.73$
Monoclinic
Cc
$a = 12.135$ (2) Å
$b = 13.572$ (1) Å
$c = 8.750$ (1) Å
$\beta = 118.37$ (1)°
$V = 1268.0$ (6) Å^3
$Z = 4$
$D_x = 1.423$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.70926$ Å
Cell parameters from 22 reflections
$\theta = 11$–20°
$\mu = 0.45$ mm^{-1}
$T = 293$ K
Irregular
$0.25 \times 0.20 \times 0.10$ mm
Colourless
Crystal source: from ethanol

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Empirical
$T_{min} = 0.69$, $T_{max} = 1.65$
1352 measured reflections
1298 independent reflections
738 observed reflections
[$I > 3\sigma(I)$]

$R_{int} = 0.012$
$\theta_{max} = 28°$
$h = -15 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 11$
2 standard reflections
frequency: 30 min
intensity variation: ±0.3%

Refinement

Refinement on F
Final $R = 0.043$
$wR = 0.044$
$S = 1.53$
738 reflections
153 parameters
H atoms refined, $U_{overall} = 0.14$ (1) Å^2

$w = (\sigma^2|F_o| + 0.0003|F_o|^2)^{-1}$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Atomic scattering factors from SHELX76

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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl	0.0672	-0.0320 (2)	0.5247	7.33 (8)
S	0.3405 (2)	0.0584 (2)	0.5244 (4)	5.38 (6)
O(1)	0.3185 (5)	-0.0444 (4)	0.4996 (9)	7.7 (2)
O(2)	0.4025 (5)	0.1082 (5)	0.4420 (8)	8.5 (3)
N(1)	-0.0001 (5)	0.1454 (4)	0.3812 (8)	4.3 (2)
N(2)	0.0412 (4)	0.2275 (4)	0.3377 (9)	5.1 (2)
N(3)	0.4254 (5)	0.0763 (4)	0.7276 (8)	4.8 (2)
C(3)	0.1606 (6)	0.2098 (5)	0.3821 (9)	4.6 (2)
C(4)	0.1958 (6)	0.1159 (5)	0.4533 (9)	4.1 (2)
C(5)	0.0907 (6)	0.0779 (5)	0.4498 (9)	4.4 (2)
C(6)	-0.1284 (6)	0.1402 (5)	0.345 (1)	4.7 (2)
C(7)	-0.1726 (7)	0.2149 (6)	0.410 (1)	5.7 (3)
C(8)	-0.2985 (8)	0.2120 (7)	0.371 (1)	7.0 (3)
C(9)	-0.3744 (8)	0.1354 (8)	0.277 (2)	7.6 (4)
C(10)	-0.3285 (7)	0.0629 (7)	0.212 (1)	7.2 (3)
C(11)	-0.2047 (7)	0.0651 (5)	0.244 (1)	5.8 (3)
C(12)	0.2357 (8)	0.2865 (6)	0.348 (1)	9.5 (4)

Table 2. Geometric parameters (Å, °)

S—O(1)	1.418 (6)	S—O(2)	1.435 (8)
S—N(3)	1.594 (7)	S—C(4)	1.744 (8)
N(1)—N(2)	1.349 (9)	N(1)—C(5)	1.34 (1)
N(1)—C(6)	1.44 (1)	N(2)—C(3)	1.33 (1)
C(3)—C(4)	1.393 (9)	C(3)—C(12)	1.50 (1)
C(4)—C(5)	1.36 (1)	C(5)—Cl	1.707 (7)
C(6)—C(7)	1.39 (1)	C(6)—C(11)	1.38 (1)
C(7)—C(8)	1.40 (1)	C(8)—C(9)	1.37 (1)
C(9)—C(10)	1.38 (1)	C(10)—C(11)	1.39 (1)
O(1)—S—O(2)	119.5 (4)	O(1)—S—N(3)	107.2 (4)
O(1)—S—C(4)	107.5 (4)	O(2)—S—N(3)	105.9 (4)
O(2)—S—C(4)	106.8 (4)	N(3)—S—C(4)	109.7 (4)
N(2)—N(1)—C(5)	110.8 (6)	N(2)—N(1)—C(6)	119.2 (6)
C(5)—N(1)—C(6)	129.9 (6)	N(1)—N(2)—C(3)	105.5 (6)
N(2)—C(3)—C(4)	110.8 (7)	N(2)—C(3)—C(12)	119.7 (7)
C(4)—C(3)—C(12)	129.5 (7)	S—C(4)—C(3)	127.7 (6)
S—C(4)—C(5)	127.7 (6)	C(3)—C(4)—C(5)	104.6 (6)
N(1)—C(5)—C(4)	108.3 (6)	N(1)—C(5)—Cl	121.3 (6)
C(4)—C(5)—Cl	130.4 (6)	N(1)—C(6)—C(7)	117.6 (7)
N(1)—C(6)—C(11)	120.4 (7)	C(7)—C(6)—C(11)	122.0 (7)
C(6)—C(7)—C(8)	118.0 (8)	C(7)—C(8)—C(9)	120.8 (9)
C(8)—C(9)—C(10)	120 (1)	C(9)—C(10)—C(11)	120.7 (9)
C(6)—C(11)—C(10)	118.5 (8)		

Data were corrected for Lp and absorption (Walker & Stuart, 1983) effects. The structure was solved by direct methods. H atoms were found in difference synthesis and included as fixed contributors with an overall isotropic thermal parameter. Programs used were: SHELXS86 (Sheldrick, 1985), SHELX76 (Sheldrick, 1976) and ORTEP (Johnson, 1965). The refinement was by blocked-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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Triphenylphosphonium Bromide

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Abstract

The structure consists of unique $[C_{18}H_{15}PH]^+Br^-$ ion pairs, which are bisected by a crystallographic mirror plane. The proton is bonded to the P atom [P—H 1.61 (9) Å] and is directed towards a Br anion [P···Br 2.20 (9) Å]. Although the structure is ionic, comparison with phosphonium bromide [$PH_4^+.Br^-$, P···Br 4.029 (4) Å; Schröder & Rush (1971). *J. Chem. Phys.*

54, 1968–1973] indicates a much greater cation–anion interaction, analogous to molecular Ph_3PBr_2 [Bricklebank, Godfrey, McAuliffe, Mackie & Pritchard (1992). *J. Chem. Soc. Chem. Commun.* pp. 355–356], which has a novel four-coordinate spoke structure with significant covalent Br—Br interaction.

Comment

The phosphonium salt reported here is an example of the type of product which can be expected if the anhydrous anaerobic conditions required for reacting metal powders with dihalophosphoranes are not rigorously maintained. The formation of triphenylphosphonium halides from triphenyldihalophosphanes in moist solvents has been reported previously (Beveridge, Harris & Payne, 1966). The title compound was isolated from the filtrate of the reaction of Ph_3PBr_2 with Cr-metal powder, which had been penetrated by moisture (Godfrey, Kelly, McAuliffe, Mackie, Matear & Pritchard, 1991). Despite their ubiquity, the only triphenylphosphonium halide structure reported to date is that of (2-hydroxyphenyl)diphenylphosphonium bromide (Schmutzler, Schomburg, Bartsch & Stelzer, 1984). The presence of the hydroxy substituent in this compound involves the P—H group in hydrogen bonding, which is impossible in the title compound.
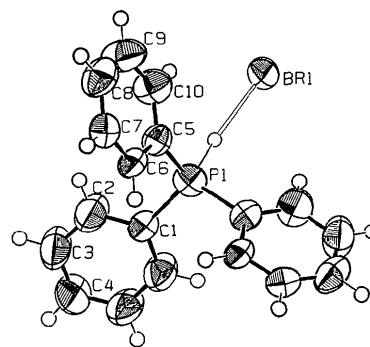

Fig. 1. The title molecule, including atomic numbering scheme, drawn using *ORTEPII* (Johnson, 1976).

Experimental

Crystal data

$C_{18}H_{16}P^+.Br^-$	Mo $K\alpha$ radiation
$M_r = 343.2$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 25
$Pnma$	reflections
$a = 10.951$ (5) Å	$\theta = 10.42$–24.52°
$b = 12.269$ (3) Å	$\mu = 2.66$ mm^{-1}
$c = 11.754$ (4) Å	$T = 296$ K
$V = 1579$ (1) Å^3	Trapezoid
$Z = 4$	$0.30 \times 0.20 \times 0.20$ mm
$D_x = 1.443$ Mg m^{-3}	Colourless