Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3732 measured reflections
3487 independent reflections
2740 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0131$
$\theta_{\rm max} = 26.91°$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: negligible

Refinement

Refinement on F^2
$R(F) = 0.0503$
$wR(F^2) = 0.1297$
$S = 1.134$
3487 reflections
302 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.3918P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.034$
$\Delta\rho_{\rm max} = 0.218$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.274$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C2	1.354 (3)	C4—C5	1.435 (3)
N1—C6	1.364 (3)	C5—C6	1.343 (3)
C2—N3	1.326 (2)	C5—C7	1.500 (3)
C2—N2	1.329 (3)	C7—C1′	1.518 (3)
N3—C4	1.347 (2)	C3′—O1	1.377 (2)
C4—N4	1.322 (2)	O1—C8	1.425 (3)
C2—N1—C6	119.8 (2)	N3—C4—C5	122.2 (2)
N3—C2—N2	120.3 (2)	C6—C5—C4	115.9 (2)
N3—C2—N1	122.4 (2)	C6—C5—C7	121.7 (2)
N2—C2—N1	117.3 (2)	C5—C7—C1′	117.9 (2)
C2—N3—C4	118.1 (2)	O1—C3′—C2′	123.8 (2)
N4—C4—N3	116.9 (2)	C3′—O1—C8	117.7 (2)
N4—C4—C5	120.9 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5	0.89 (3)	1.91 (3)	2.798 (2)	175 (3)
N2—H2*A*···O4	0.93 (3)	1.91 (3)	2.827 (3)	171 (2)
N2—H2*B*···O1$^{\rm i}$	0.85 (3)	2.21 (3)	2.979 (2)	150 (3)

Symmetry code: (i) $1 + x, y, 1 + z$.

H atoms were located from a difference Fourier map and their coordinates and isotropic displacement parameters were refined.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93 and *PARST* (Nardelli, 1983).

SM acknowledges UGC for a Junior Research Fellowship. PTM is a Career Awardee of UGC. The authors thank the National Diffractometer Facility (a DST-funded facility) at the Biophysics Department, AIIMS, New Delhi, for X-ray data collection.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: VJ1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(2-Fluorophenyl)- and 1-(3-Fluorophenyl)-1*H*,3*H*-thiazolo[3,4-*a*]benzimidazole

Giuseppe Bruno,[a] Silvana Grasso,[b] Pietro Monforte,[b] Francesco Nicoló[a] and Rosario Scopelliti[a]

[a]*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Universitá di Messina, 98166 Vill. Sant'Agata, Messina, Italy, and* [b]*Dipartimento Farmaco–Chimico, Universitá di Messina, 98168 Viale Annunziata, Messina, Italy. E-mail: bruno@medif0.unime.it*

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Abstract

In the solid-state structures of the title compounds, $C_{15}H_{11}FN_2S$, with 2-fluorophenyl and 3-fluorophenyl substituents, the thiazole ring shows the typical envelope conformation, while the benzimidazole system is planar.

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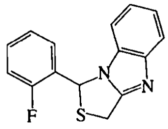
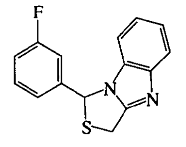
Comment

In recent years there has been considerable interest in the synthesis and characterization of drugs for the treatment of AIDS. In previous papers (Chimirri, Grasso, Monforte, Monforte & Zappalá, 1991*a*,*b*; Bruno *et al.*, 1997), we reported that several 1-aryl-substituted 1*H*,3*H*-thiazolo[3,4-*a*]benzimidazoles exhibited good anti-HIV activity. In particular, it was found that the presence of one or two F atoms on the phenyl ring at C1 leads to the most active compounds of the series. In this context, the X-ray structure determinations of 1-(2-fluorophenyl)-1*H*,3*H*-thiazolo[3,4-*a*]benzimidazole, (1), and 1-(3-fluorophenyl)-1*H*,3*H*-thiazolo[3,4-*a*]benzimidazole, (2), were carried out in order to observe whether the different positions of the substituent affect the geometry of the molecule.



(1)



(2)

Both compounds assume a butterfly-like conformation similar to that described in an analogous molecule (Bruno, Monforte, Nicoló, Scopelliti & Zappalá, 1996); this is evidenced by the angles between the planes formed by the phenyl substituent at C1 and the thiazolobenzimidazole system (except S) [71.71 (4) for compound (1) and 76.79 (5)° for compound (2)], and by the N2—C1—C10—C11 torsion angles [34.8 (2) for (1) and 42.9 (2)° for (2)]. Both compounds are racemates.

As expected, the benzimidazole system in both compounds is planar due to the wide electronic delocalization effect [maximum deviations 0.012 (2) and 0.010 (2) Å for C3 in (1) and (2), respectively]. The S atom lies 0.308 (1) and 0.309 (1) Å from the weighted least-squares plane defined by the remaining atoms of the three fused rings in (1) and (2), respectively. Furthermore, the stereochemistry of the molecule allows the S atom to lie on the same side as the phenyl substituent at the C1 atom and in both molecules it has a large U_{22} displacement parameter. The C9—S—C1 angles are in good agreement with those found for similar molecules. The lengthening of the S1—C1 bond distance [average value 1.848 (2) Å] *versus* the S1—C9 bond distance [average value 1.819 (2) Å] in both compounds may be described in terms of the steric effect of the phenyl substitutent at C1. The thiazole ring assumes a slightly distorted envelope conformation in both compounds [φ = −9.3 (5)° for (2) and −12.5 (4)° for (1) (Cremer & Pople, 1975)].

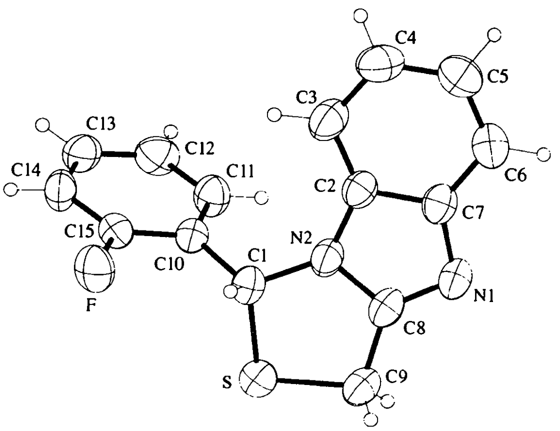


Fig. 1. The molecular structure of (1). Displacement ellipsoids are drawn at the 50% probability level.

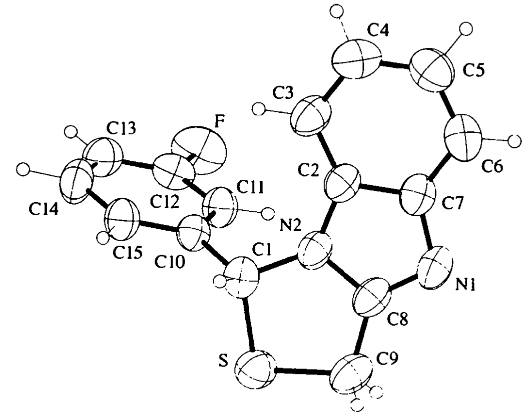


Fig. 2. The molecular structure of (2). Displacement ellipsoids are drawn at the 50% probability level.

In compound (1), there is only one intermolecular hydrogen interaction [F$\cdots$H12$^{\rm iii}$ 2.49 (2), F$\cdots$C12$^{\rm iii}$ 3.432 (2) Å and F$\cdots$H12$^{\rm iii}$—C12$^{\rm iii}$ 162 (2)°; symmetry code: (iii) x, $-1+y$, z] and the same atom is involved in an intramolecular hydrogen interaction [F$\cdots$H1 2.39 (2), F$\cdots$C1 2.787 (2) Å and F$\cdots$H1—C1 104 (1)°]. In compound (2), the F atom of the phenyl substitutent is involved in two intermolecular interactions, one being similar to that observed for compound (1) [F$\cdots$H15$^{\rm i}$ 2.44 (2), F$\cdots$C15$^{\rm i}$ 3.357 (2) Å and F$\cdots$H15$^{\rm i}$—C15$^{\rm i}$ 168 (2)°; F$\cdots$H5$^{\rm ii}$ 2.53 (2), F$\cdots$C5$^{\rm ii}$ 3.165 (3) Å and F$\cdots$H5$^{\rm ii}$—C5$^{\rm ii}$ 121 (2)°; symmetry codes: (i) x, $1+y$, z; (ii) $1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$]. In the crystalline state, there is also a graphitic interaction between molecules related by an inversion centre; these show the typical head-to-tail disposition and the distance between planes is 3.643 (1) for (1) and 3.519 (2) Å for (2). Both compounds are, from a stereochemical point of view, virtually identical.

Experimental

Both compounds were synthesized as described in Chimirri, Grasso, Monforte, Monforte & Zappalá (1991*a*), and recrystallized from ethanol.

Compound (1)

Crystal data

$C_{15}H_{11}FN_2S$
$M_r = 270.32$
Monoclinic
$P2_1/c$
$a = 11.344\,(1)$ Å
$b = 7.437\,(1)$ Å
$c = 15.542\,(2)$ Å
$\beta = 108.390\,(10)°$
$V = 1244.2\,(3)$ Å^3
$Z = 4$
$D_x = 1.443$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 6.57–14.45°$
$\mu = 0.258$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
$0.20 \times 0.18 \times 0.16$ mm
Yellow

Data collection

Siemens *R3m/V* diffractometer
$\omega–2\theta$ scans
Absorption correction: none
5826 measured reflections
2210 independent reflections
1667 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0170$
$\theta_{\rm max} = 25.05°$
$h = -13 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 18$
3 standard reflections every 197 reflections intensity decay: 0.82%

Refinement

Refinement on F^2
$R(F) = 0.0288$
$wR(F^2) = 0.0750$
$S = 0.933$
2210 reflections
217 parameters
H atoms freely refined with $U_{\rm iso}$
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$

$\Delta\rho_{\rm max} = 0.161$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.157$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0004 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S—C9	1.818 (2)	C8—N1	1.305 (2)
S—C1	1.849 (2)	C8—C9	1.490 (2)
C1—N2	1.450 (2)	C2—C7	1.403 (2)
N2—C8	1.364 (2)	C7—N1	1.402 (2)
N2—C2	1.388 (2)		
C9—S—C1	94.44 (8)	N2—C8—C9	114.15 (15)
N2—C1—S	102.30 (11)	C8—C9—S	105.05 (12)
C8—N2—C2	106.97 (14)	N2—C2—C7	104.17 (14)
C8—N2—C1	119.33 (14)	N1—C7—C2	110.85 (14)
N1—C8—N2	114.23 (14)	C8—N1—C7	103.76 (13)

Compound (2)

Crystal data

$C_{15}H_{11}FN_2S$
$M_r = 270.32$
Monoclinic
$P2_1/c$
$a = 11.249\,(1)$ Å
$b = 7.421\,(1)$ Å
$c = 15.867\,(2)$ Å
$\beta = 107.56\,(1)°$
$V = 1262.8\,(3)$ Å^3
$Z = 4$
$D_x = 1.422$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 6.82–17.06°$
$\mu = 0.254$ mm^{-1}
$T = 293\,(2)$ K
Prismatic
$0.28 \times 0.26 \times 0.13$ mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
$\omega–2\theta$ scans
Absorption correction: none
2908 measured reflections
2232 independent reflections
1722 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0109$
$\theta_{\rm max} = 25.04°$
$h = -13 \rightarrow 12$
$k = -1 \rightarrow 8$
$l = -1 \rightarrow 18$
3 standard reflections every 197 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0347$
$wR(F^2) = 0.1011$
$S = 1.049$
2232 reflections
217 parameters
H atoms freely refined with $U_{\rm iso}$
$w = 1/[\sigma^2(F_o^2) + (0.065P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$

$\Delta\rho_{\rm max} = 0.346$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.206$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0006 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S—C9	1.820 (2)	C8—N1	1.308 (2)
S—C1	1.846 (2)	C8—C9	1.490 (3)
C1—N2	1.453 (2)	C2—C7	1.402 (3)
N2—C8	1.359 (2)	C7—N1	1.396 (3)
N2—C2	1.382 (2)		
C9—S—C1	94.69 (9)	N2—C8—C9	114.3 (2)
N2—C1—S	102.48 (12)	C8—C9—S	105.04 (13)
C8—N2—C2	107.24 (14)	N2—C2—C7	104.1 (2)
C8—N2—C1	119.7 (2)	N1—C7—C2	110.9 (2)
N1—C8—N2	114.0 (2)	C8—N1—C7	103.72 (15)

For both compounds, data collection: *P3/V Control Software* (Siemens, 1989); cell refinement: *P3/V Control Software*; data reduction: *SHELXTL-Plus* (Sheldrick, 1991); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *PARST*95 (Nardelli, 1995) and *SHELXL*93.

We would like to express our gratitude, for support and aid, to the Italian MURST and the 'Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi X' of the University of Messina.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1149). 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**, 767–768

7,8-Bis(pyridinium-2-ylthio)-7,8-dicarba-*nido*-undecaborate Trifluoromethanesulfonate

PETER G. JONES,[a] OLGA CRESPO,[b] M. CONCEPCIÓN GIMENO[b] AND ANTONIO LAGUNA[b]

[a]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and* [b]*Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza–CSIC, 50009 Zaragoza, Spain. E-mail: jones@xray36.anchem.nat.tu-bs.de*

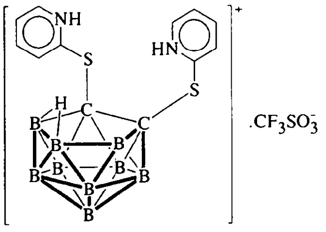
(*Received 27 September 1996; accepted 7 February 1997*)

Abstract

In the title compound, $C_{12}H_{20}B_9N_2S_2^+.CF_3SO_3^-$, the open B_3C_2 face of the carborane contains three terminal H atoms and one bridging B—H—B unit, with B—H distances of 1.12 (3) and 1.39 (3) Å. The S—C—C/N angles to the pyridinium groups differ appreciably, possibly because of H···H steric interactions between pyridinium and carborane. Hydrogen bonds of the form N—H···O link two anions and two cations over an inversion centre.

Comment

We are interested in ligands based on the partially degraded 1,2-dicarba-*closo*-dodecaborane derivatives, the 7,8-dicarba-*nido*-undecaborates, *e.g.* the 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate anion $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and its transition metal complexes (Jones, Villacampa, Crespo, Gimeno & Laguna, 1997; Crespo, Gimeno, Jones & Laguna, 1996, and references therein). We have also begun to study related sulfur-containing ligands and present here the structure of the zwitterionic salt 7,8-bis(pyridinium-2-ylthio)-7,8-dicarba-*nido*-undecaborate trifluoromethanesulfonate, (I).



(I)

As can be seen in Fig. 1, atoms C7, C8, S1 and S2 are approximately coplanar (mean deviation 0.06 Å), but the pyridinium groups point to opposite sides of this plane, with C21—S2···S1—C11 130.7 (1)°. The C—S bond lengths of 1.778 and 1.782 (2) Å to the carborane and of 1.749 and 1.765 (2) Å to the pyridinium groups may be regarded as normal. The C—S—C angles differ appreciably [102.3 (1) at S1 and 107.5 (1)° at S2] for no obvious reason; the major differences in the S—C—N/C angles [S1—C11—N16 114.8 and S2—C21—N26 116.2 (2)° *cf.* S1—C11—C12 127.3 and S2—C21—C22 125.5 (2)°] may be attributed to unfavourable steric interactions between the H11 or H22 atoms and the carborane unit [H12···H10*B* 2.22 and H22···H2 2.54 Å].

We have determined the structures of seven heavy-atom derivatives of the above-mentioned diphosphine (references above and unpublished work). The light-atom (B/C) positions were necessarily imprecise and the carborane H-atom positions extremely imprecise. How-

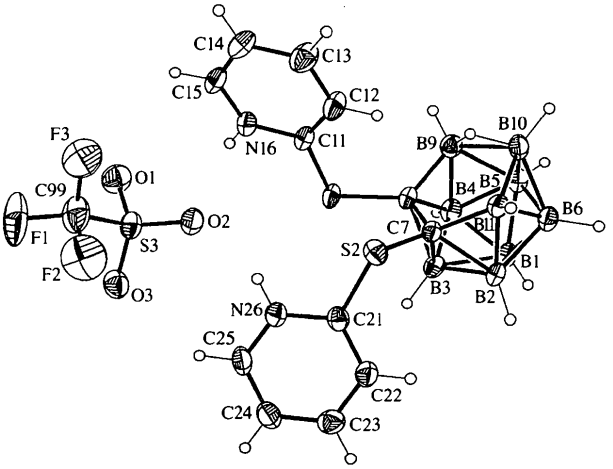


Fig. 1. The ionic title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

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