4,7-Bis(4-pyridylethynyl)-2,1,3-benzo-thiadiazole and its dipyridinium diperchlorate

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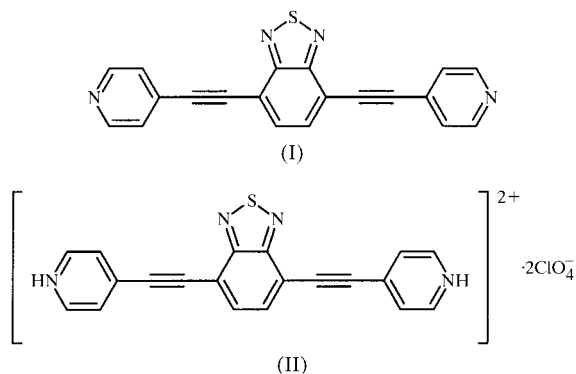Correspondence e-mail: tomura@ims.ac.jp

The title compound, $C_{20}H_{10}N_4S$, and its dipyridinium salt, 4,4'-(2,1,3-benzodiazol-4,7-diyldiethynyl)dipyridinium diperchlorate, $C_{20}H_{12}N_4S^{2+}·2ClO_4^{-}$, display bond alternation in the 2,1,3-benzothiadiazole rings, which suggests their quinonoid character. The dipyridinium dication molecules stack along the a axis and form a dimer with short $S··· N$ interheteroatom contacts [3.146 (4) Å] between the two 1,2,5-thiadiazole rings. The dimer is surrounded by the perchlorate anions with which it forms a large number of intermolecular $N—H··· O$ and $C—H··· O$ hydrogen bonds.

Comment

Long rigid and conjugated bridging ligands have received much current interest with regard to the construction of self-assembling macrocyclic architectures (Lehn, 1995; Fujita, 1999) and the development of molecular wires (Tour, 1996). Additionally, incorporation of redox-active and/or luminescent parts into the ligands is attractive for exploring functional

(I)

(II)

supramolecular systems (Hock *et al.*, 1996; Sun & Lees, 2000). With this in mind, we have recently synthesized a novel ligand with a 2,1,3-benzothiadiazole ring and two terminal pyridine rings, namely 4,7-bis(4-pyridylethynyl)-2,1,3-benzothiadiazole,

(I). The S and N atoms in the 1,2,5-thiadiazole ring of (I) are expected to form short interheteroatom contacts which can result in unique molecular networks (Yamashita & Tomura, 1998). In the course of our studies on (I), we have also isolated its dipyridinium salt, 4,4'-(2,1,3-benzodiazol-4,7-diyldiethynyl)dipyridinium diperchlorate, (II), as single crystals. We report here the molecular and unique crystal structures of (I) and (II).

Compounds (I) and (II) crystallize in the $P2_1/a$ and $P2_1/c$ space groups, respectively, with one molecule in the asymmetric unit. The molecular structures of (I) and (II) are shown in Figs. 1 and 2, and selected geometric parameters are listed in Tables 1 and 2, respectively. Compound (I) and the dipyridinium dication in (II) generally have similar molecular geometries. They are long linear molecules with lengths of 16.557 (5) Å for (I) and 16.387 (6) Å for (II) (N3··· N4 distance). The dipyridinium dication of (II) is more linear [C8—C7—C1 179.4 (6) and C15—C14—C4 178.7 (5)°], while (I) bends slightly [C8—C7—C1 176.2 (4) and C15—C14—C4 174.4 (5)°]. The 2,1,3-benzothiadiazole and two pyridine rings are planar within 0.026 (3) Å for (I) and 0.038 (4) Å for (II). Compound (I) lies in a plane (r.m.s. deviation of fitted atoms 0.1043 Å) and the angles between the 2,1,3-benzothiadiazole and two pyridine rings are 1.5 (2)° (C9—C10—C11—N3—C12—C13) and 11.6 (2)° (C16—C17—C18—N4—C19—C20). In the dipyridinium dication in (II), the 2,1,3-benzothiadiazole and one pyridine ring (C9—C10—C11—N3—C12—C13) are almost coplanar [r.m.s. deviation of fitted atoms is 0.0541 Å and the angle between the planes of the two rings is 5.4 (3)°], while the other pyridine ring tilts toward the 2,1,3-benzothiadiazole, with an angle of 44.5 (2)°. The C1—C7, C8—C9,
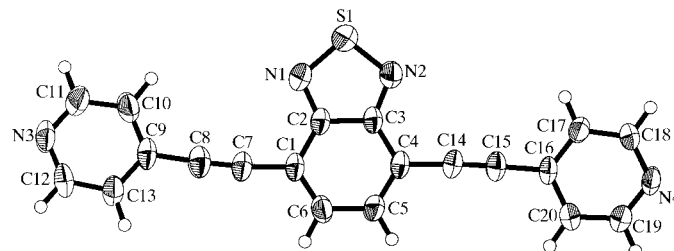
Figure 1
The molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
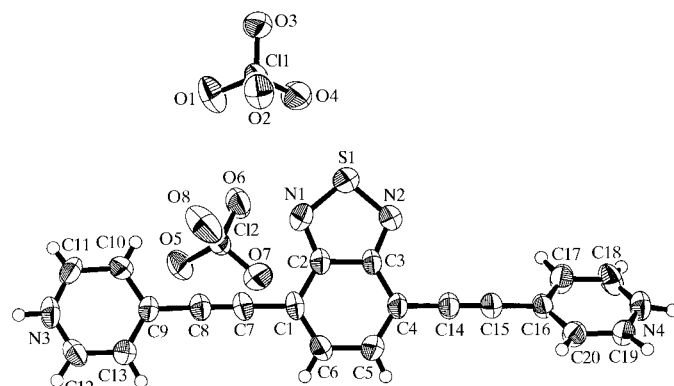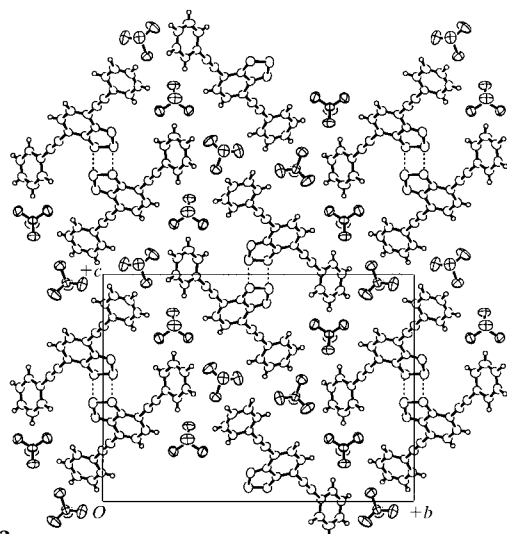

Figure 2
The molecular structure of (II) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

C4—C14 and C15—C16 bonds [1.429 (4)–1.445 (4) Å for (I) and 1.428 (6)–1.438 (6) Å for (II)] are almost the same length as the typical $C_{aromatic}$—Csp bond, *i.e.* 1.434 Å (Allen *et al.*, 1987).

There is considerable shortening of the C1—C6 and C4—C5 bonds compared with the other bonds in the benzene rings of (I) and (II). Such double-bond fixation suggests a quinonoid character of the 2,1,3-benzothiadiazole ring in (I) and (II). The geometric parameters of the 1,2,5-thiadiazole rings in (I) and (II) are almost the same as those of 3,4-diphenyl-1,2,5-thia-diazole (Mellini & Merlino, 1976).

Fig. 3 shows the packing diagram of (II) viewed along the *a* axis. The dipyridinium dication molecules form single stacks along the *a* axis. The interstack distance (distance between the two 2,1,3-benzothiadiazole ring planes within the stack) is 3.40 (1) Å. The most remarkable feature of the crystal structure of (II) is the existence of short S···N interheteroatom contacts [3.146 (4) Å for S1···N2^i and N2···S1^i; symmetry code: (i) $-x$, $-y + 1$, $-z$] between the two 1,2,5-thiadiazole rings. The S···N distance is 6.1% shorter, and the S1···S1^i [3.960 (3) Å] and N2···N2^i [3.048 (8) Å] distances between the 1,2,5-thiadiazole rings are 6.5 and 1.6% longer, respectively, than the sum of the corresponding van der Waals radii (Pauling, 1960). Thus, the dipyridinium dication molecules form a dimer with short S···N contacts, which is planar and lies in a plane within a deviation of 0.09 (1) Å. No short S···N interheteroatom contact within the sum of the van der Waals radii of the S and N atoms was observed in the crystal structure of (I) [the shortest S···N interheteroatom contact was S1···N4($-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + 1$) 3.380 (3) Å]. Interestingly, the dimer is surrounded by the perchlorate anions, as shown in Fig. 3. A large number of intermolecular N—H···O and C—H···O hydrogen bonds (Taylor & Kennard, 1982; Biradha *et al.*, 1993; Batchelor *et al.*, 2000) are observed between the dipyridinium dication and the O atoms of the perchlorate anions (see Table 3). The intermolecular O···O distances of the perchlorates are in the range 3.044 (6)–3.286 (6) Å.

Studies on the construction of new molecular architectures using compound (I) are now in progress.

Experimental

Compound (I) was synthesized by the reaction of 4,7-dibromo-2,1,3-benzothiadiazole (Pilgram *et al.*, 1970) with 4-ethynylpyridine (Ciana & Haim, 1984). To a solution of 4-ethynylpyridine (1.63 g, 15.9 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (2.00 g, 6.8 mmol) in triethyl-amine (150 ml), bis(triphenylphosphine)palladium(II) dichloride (0.115 g, 0.164 mmol) and copper(I) bromide (0.101 g, 0.702 mmol) were added. After stirring for 30 min at 333 K, the reaction mixture was stirred for 2 d at 363 K under argon. Triethylamine was removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The solution was washed with aqueous K_2CO_3 and dried over Na_2SO_4. After the solvent was evaporated *in vacuo*, the crude product (yield 1.79 g, 78%) was purified by sublimation [453–473 K, 10^{-2} Torr (1 Torr = 133.322 Pa)] to give (I) as a yellow powder. Slow evaporation of a solution of (I) in CH_2Cl_2–ethyl acetate (5:1) afforded yellow crystals of (I) suitable for X-ray analysis. Physical data for (I): m.p. 523–525 K; ^{1}H NMR (CDCl$_3$, 270 MHz): δ 7.55 (*d*), 7.88 (*s*), 8.69 (*d*); MS (EI): *m/z* 338 (*M*$^+$). Slow evaporation of a solution of (I) with copper(II) perchlorate in CH_2Cl_2–ethyl acetate (5:1) gave orange crystals of (II) suitable for X-ray analysis.

Compound (I)

Crystal data

$C_{20}H_{10}N_4S$	$D_x = 1.411$ Mg m^{-3}
$M_r = 338.38$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 25
$a = 12.487$ (2) Å	reflections
$b = 7.5477$ (13) Å	$\theta = 18.7$–$42.4°$
$c = 17.513$ (3) Å	$\mu = 1.88$ mm^{-1}
$\beta = 105.22$ (2)°	$T = 296$ (2) K
$V = 1592.8$ (5) Å^3	Prismatic, yellow
$Z = 4$	$0.50 \times 0.30 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffrac-tometer	$R_{int} = 0.079$
ω–2θ scans	$\theta_{max} = 74.3°$
Absorption correction: ψ scan	$h = -15 \rightarrow 0$
(North *et al.*, 1968)	$k = -9 \rightarrow 0$
$T_{min} = 0.454$, $T_{max} = 0.835$	$l = -21 \rightarrow 21$
3416 measured reflections	3 standard reflections
3254 independent reflections	frequency: 120 min
1902 reflections with $I > 2\sigma(I)$	intensity decay: 2.4%

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

S1—N1	1.611 (3)	C3—C4	1.430 (5)
S1—N2	1.613 (4)	C4—C5	1.365 (5)
N1—C2	1.338 (5)	C4—C14	1.445 (4)
N2—C3	1.334 (5)	C5—C6	1.426 (5)
C1—C6	1.376 (5)	C7—C8	1.183 (4)
C1—C2	1.424 (5)	C8—C9	1.429 (4)
C1—C7	1.444 (4)	C14—C15	1.170 (5)
C2—C3	1.441 (4)	C15—C16	1.442 (5)
N1—S1—N2	100.83 (17)	C4—C3—C2	120.5 (3)
C2—N1—S1	106.7 (2)	C5—C4—C3	117.5 (3)
C3—N2—S1	106.5 (2)	C5—C4—C14	124.1 (4)
C6—C1—C2	117.6 (3)	C3—C4—C14	118.4 (3)
C6—C1—C7	121.7 (3)	C4—C5—C6	122.2 (4)
C2—C1—C7	120.7 (3)	C1—C6—C5	122.0 (4)
N1—C2—C1	127.1 (3)	C8—C7—C1	176.2 (4)
N1—C2—C3	112.8 (3)	C7—C8—C9	178.5 (5)
C1—C2—C3	120.2 (3)	C15—C14—C4	174.4 (5)
N2—C3—C4	126.3 (3)	C14—C15—C16	177.1 (5)
N2—C3—C2	113.2 (3)		

Figure 3
Packing diagram of (II) viewed along the *a* axis. Dotted lines show the short S···N interheteroatom contacts.

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.068$

$wR(F^2) = 0.209$

$S = 1.07$

3254 reflections

226 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1016P)^2 + 0.5079P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.69$ e Å^{-3}

$\Delta\rho_{min} = -0.33$ e Å^{-3}

Compound (II)

Crystal data

$C_{20}H_{12}N_4S^{2+}\cdot2ClO_4^-$

$M_r = 539.30$

Monoclinic, $P2_1/c$

$a = 5.1097$ (3) Å

$b = 24.4522$ (16) Å

$c = 17.8489$ (13) Å

$\beta = 92.281$ (5)°

$V = 2228.3$ (3) Å^3

$Z = 4$

$D_x = 1.608$ Mg m^{-3}

Cu $K\alpha$ radiation

Cell parameters from 25 reflections

$\theta = 15.9$–$42.4°$

$\mu = 4.02$ mm^{-1}

$T = 296$ (2) K

Plate, orange

$0.35 \times 0.15 \times 0.05$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer

ω–2θ scans

Absorption correction: ψ scan (North *et al.*, 1968)

$T_{min} = 0.334$, $T_{max} = 0.824$

4684 measured reflections

4543 independent reflections

2774 reflections with $I > 2\sigma(I)$

$R_{int} = 0.062$

$\theta_{max} = 74.3°$

$h = -6 \rightarrow 6$

$k = 0 \rightarrow 30$

$l = -22 \rightarrow 0$

3 standard reflections

frequency: 120 min

intensity decay: 0.4%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.205$

$S = 1.00$

4543 reflections

364 parameters

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1212P)^2 + 0.9345P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.53$ e Å^{-3}

$\Delta\rho_{min} = -0.37$ e Å^{-3}

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

S1—N2	1.608 (4)	C3—C4	1.405 (6)
S1—N1	1.617 (4)	C4—C5	1.367 (7)
N1—C2	1.330 (6)	C4—C14	1.438 (6)
N2—C3	1.335 (6)	C5—C6	1.424 (7)
C1—C6	1.375 (7)	C7—C8	1.188 (6)
C1—C2	1.426 (6)	C8—C9	1.428 (6)
C1—C7	1.434 (6)	C14—C15	1.188 (6)
C2—C3	1.440 (5)	C15—C16	1.435 (6)
N2—S1—N1	100.4 (2)	C4—C3—C2	120.4 (4)
C2—N1—S1	106.6 (3)	C5—C4—C3	118.9 (4)
C3—N2—S1	107.1 (3)	C5—C4—C14	121.8 (4)
C6—C1—C2	118.2 (4)	C3—C4—C14	119.3 (4)
C6—C1—C7	121.0 (4)	C4—C5—C6	121.4 (5)
C2—C1—C7	120.7 (4)	C1—C6—C5	121.5 (5)
N1—C2—C1	127.1 (4)	C8—C7—C1	179.4 (6)
N1—C2—C3	113.3 (4)	C7—C8—C9	179.3 (6)
C1—C2—C3	119.6 (4)	C15—C14—C4	178.7 (5)
N2—C3—C4	127.0 (4)	C14—C15—C16	179.1 (5)
N2—C3—C2	112.6 (4)		

All H atoms of (I) were placed in geometrically calculated positions (C—H = 0.93 Å) and refined using a riding model. All H atoms of (II) were localized in the Fourier map and refined isotropically [C—H = 0.80 (5)–0.96 (5) Å].

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$\cdots$O6[i]	0.88 (7)	1.97 (7)	2.843 (5)	171 (4)
N4—H4$\cdots$O8[ii]	0.91 (6)	2.18 (6)	2.975 (6)	145 (5)
C5—H5$\cdots$O3[iii]	0.87 (5)	2.73 (6)	3.314 (7)	126 (3)
C10—H10$\cdots$O4[iv]	0.83 (5)	2.57 (5)	3.299 (7)	148 (3)
C11—H11$\cdots$O1[iv]	0.80 (5)	2.73 (5)	3.307 (7)	131 (4)
C11—H11$\cdots$O2[i]	0.80 (5)	2.61 (5)	3.341 (6)	153 (4)
C12—H12$\cdots$O7[v]	0.94 (5)	2.49 (5)	3.162 (7)	129 (3)
C12—H12$\cdots$O7[i]	0.94 (5)	2.62 (5)	3.317 (7)	132 (3)
C13—H13$\cdots$O5[v]	0.92 (4)	2.55 (4)	3.358 (6)	147 (2)
C13—H13$\cdots$O7[vi]	0.92 (4)	2.69 (4)	3.306 (7)	125 (2)
C17—H17$\cdots$O4[vii]	0.93 (6)	2.74 (6)	3.382 (7)	127 (4)
C18—H18$\cdots$O1[vii]	0.84 (6)	2.43 (6)	3.223 (7)	157 (4)
C18—H18$\cdots$O3[viii]	0.84 (6)	2.75 (6)	3.177 (6)	113 (4)
C18—H18$\cdots$O4[viii]	0.84 (6)	2.84 (6)	3.230 (7)	110 (4)
C19—H19$\cdots$O2[ii]	0.95 (6)	2.69 (5)	3.273 (6)	120 (3)
C19—H19$\cdots$O6[ii]	0.95 (6)	2.46 (6)	3.378 (7)	162 (3)
C19—H19$\cdots$O8[ii]	0.95 (6)	2.84 (5)	3.305 (6)	111 (3)
C20—H20$\cdots$O1[iii]	0.88 (5)	2.54 (5)	3.370 (7)	159 (3)
C20—H20$\cdots$O2[ii]	0.88 (5)	2.87 (5)	3.348 (6)	116 (3)

Symmetry codes: (i) $2 + x, y, z$; (ii) $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $1 + x, y, z$; (v) $2 - x, 1 - y, 1 - z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $-x, 1 - y, -z$; (viii) $-1 - x, 1 - y, -z$.

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

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