Acta Cryst. (1999). C55, 1890–1892

Centrosymmetric molecular strings in the hydrogen-bonded structure of 4,4′-bipyridyl–4,4′-thiodiphenol (3/2)

Alan J. Lough,[a] Richard M. Gregson,[b] George Ferguson[b]† and Christopher Glidewell[b]

[a]*Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 3H6, and* [b]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland. E-mail: cg@st-andrews.ac.uk*

(*Received 26 May 1999; accepted 30 June 1999*)

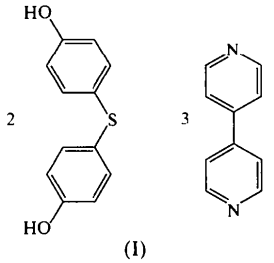
Abstract

The title compound, $3C_{10}H_8N_2{\cdot}2C_{12}H_{10}O_2S$, contains five-component molecular strings lying across centres of inversion and containing alternating 4,4′-bipyridyl and 4,4′-thiodiphenol units; the molecular components are linked by just two types of O—H···N hydrogen bonds [O···N 2.736 (2) and 2.683 (2) Å; O—H···N 162 and 169°]. Each string is connected to two neighbouring strings by means of aromatic $\pi\cdots\pi$ stacking interactions across centres of inversion to give continuous chains running parallel to $[10\bar{1}]$.

Comment

In supramolecular compounds, the bis-phenol 4,4′-thiodiphenol, $S(C_6H_4OH)_2$, invariably acts as a double donor of hydrogen bonds, with neither O nor S acting as hydrogen-bond acceptors. Thus, in combination with double acceptors of hydrogen bonds, this bis-phenol is expected to act as a chain-building unit (Coupar *et al.*, 1996*b*, 1997; Ferguson *et al.*, 1997). Similarly 4,4′-bipyridyl, $NC_5H_4{-}C_5H_4N$, generally acts as a double acceptor of hydrogen bonds (Coupar *et al.*, 1996*a*; Bényei *et al.*, 1998; Ferguson, Glidewell, Gregson & Lavender, 1999; Lavender *et al.*, 1999; Wheatley *et al.*, 1999). However, sometimes only one of the N atoms is active in hydrogen bonding, as in the salt formed with phenylphosphonic acid (Ferguson *et al.*, 1998), while in the adduct formed with ferrocene-1,1′-diylbis(diphenylmethanol), $Fe(C_5H_4CPh_2OH)_2$, one half of the 4,4′-bipyridyl units act as double acceptors, while the remainder do not participate at all in the hydrogen bonding (Glidewell *et al.*, 1994). Thus, in its action as a double acceptor of hydrogen bonds, this diamine is a potential chain-building unit, while as a single acceptor, it is a potential chain terminator; in this dual function, 4,4′-bipyridyl bears some resemblance to 1,10-phenanthroline (Ferguson, Glidewell & Lavender, 1999).

In this paper, we report the synthesis and structural characterization of the 3:2 adduct formed between 4,4′-bipyridyl and 4,4′-thiodiphenol, *i.e.* $3C_{10}H_8N_2{\cdot}2C_{12}H_{10}O_2S$, (I), in which the chain-building and chain-terminating characteristics of 4,4′-bipyridyl are both evident.



(I)

Compound (I) crystallizes in $P2_1/c$ in a unit cell of unusual tabular shape, with one molecule of the bipyridyl and one of the bis-phenol lying in general positions, together with one molecule of the bipyridyl lying across a centre of inversion, thus giving a 3:2 molar ratio of bipyridyl to bis-phenol (Fig. 1). These molecular units are linked by just two types of O—H···N hydrogen bond into fully extended five-molecule strings (Fig. 2). Within the asymmetric unit (Fig. 1), O14 acts as hydrogen-bond donor to N31 in the 4,4′-bipyridyl unit lying across the centre of inversion at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and O24 acts as hydrogen-bond donor to N41 in the other independent bipyridyl (Table 2); N51 does not act as a hydrogen-bond acceptor. Hence, the centrosymmetric 4,4′-bipyridyl unit is acting as a chain builder and the other bipyridyl, containing N41 and N51, is acting as a chain terminator. Two of these five-molecule strings, related to one another by the action of the glide plane, lie in each unit cell. The two independent O—H···N hydrogen bonds are both short (Table 2), but there is no evidence at all for any proton transfer from O to N. In the standard $P2_1/c$ setting, and with the molecular string centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, the string runs approximately along the long diagonal of the (010) projection of the tabular unit cell, and it is some 40 Å in length.

The heteroaromatic ring containing N51 (the N atom not involved in the hydrogen bonding) at (x, y, z) and the analogous ring at ($-x$, $1-y$, $2-z$) are linked by aromatic $\pi\cdots\pi$ stacking interactions across the centre of inversion at $(0,\frac{1}{2},1)$, characterized by a perpendicular separation of 3.33 (2) Å and a centroid offset of 1.77 (2) Å. The symmetry-related ring, N51–C56, in the same molecular aggregate is at ($1-x$, $1-y$, $1-z$), and this forms a $\pi\cdots\pi$ stacking interaction with the corresponding ring at ($1-x$, y, $-1+z$) across the inversion centre at $(1,\frac{1}{2},0)$. The 4,4′-bipyridyl units at ($-x$, $1-y$, $2-z$) and ($1+x$, y, $-1+z$) are components of the

---

† On leave from the Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

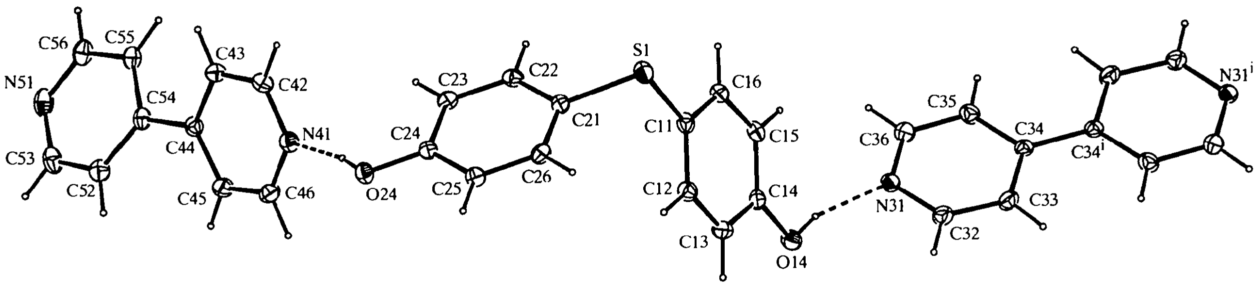


Fig. 1. A view of the unique molecular components of (I) showing the atom-labelling scheme [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$]. Displacement ellipsoids are drawn at the 30% probability level.

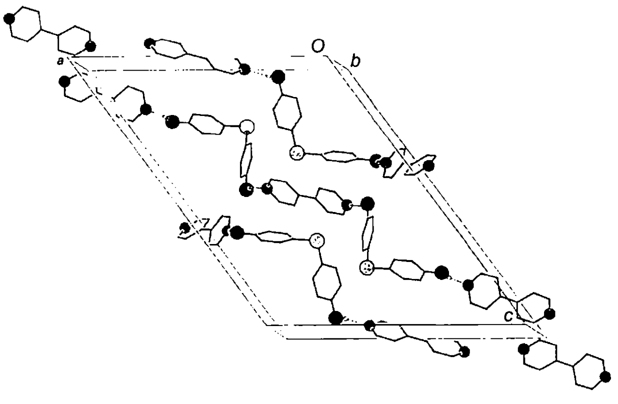


Fig. 2. Part of the crystal structure of (I) showing the unit-cell contents, including one of the five-molecule strings, together with terminal bipyridyl units [symmetry positions ($-x$, $1 - y$, $2 - z$) and ($1 + x$, y, $-1 + z$)] from two neighbouring strings, illustrating the centrosymmetric $\pi \cdots \pi$ stacking. For the sake of clarity, H atoms bonded to C have been omitted, and dark, intermediate and light shading indicates N, O and S atoms, respectively.

molecular aggregates centred at $(-\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ and $(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2})$, respectively, so that the combination of O—H$\cdots$N hydrogen bonds and aromatic $\pi \cdots \pi$ stacking interactions links the individual molecular components into continuous chains running parallel to the $[10\bar{1}]$ direction. There is a second chain running through the cell, in the (010) projection offset from the first by a displacement of $c/2$; there are no hydrogen-bonding interactions between the individual chains less than the sum of the van der Waals distances.

The 4,4′-thiodiphenol molecule in (I) has a conformation remote from C_{2v} symmetry or from any subgroup of C_{2v} (Table 1); the dihedral angles between the central C11—S1—C21 plane and those of the two aryl groups are 55.7 (1) and 88.8 (1)°. The two rings in the centrosymmetric 4,4′-bipyridyl unit are necessarily parallel, but they are not quite coplanar; the molecule is stepped with a perpendicular riser of 0.028 (2) Å. In the other 4,4′-bipyridyl unit, the dihedral angle between the two ring planes is 25.8 (1)°. The O—C—C angles in the 4,4′-thiodiphenol component show the usual dependence on the orientation of the hydroxyl-H atoms; the C—N—C angles in the 4,4′-bipyridyl components are all significantly less than 120°.

Examination of the structure with *PLATON* (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

Experimental

Samples of 4,4′-bipyridyl and 4,4′-thiodiphenol were dissolved separately in methanol–acetone (50/50 *v*/*v*) and aliquots of these solutions were mixed to give a 2:1 molar ratio of bipyridyl to bis-phenol. This mixture was set aside to crystallize, yielding analytically pure (I). Analysis, found: C 71.3, H 4.9, N 9.6%; $C_{54}H_{44}N_6O_4S_2$ requires: C 71.7, H 4.9, N 9.3%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$3C_{10}H_8N_2 \cdot 2C_{12}H_{10}O_2S$
$M_r = 905.09$
Monoclinic
$P2_1/c$
$a = 19.7378\,(10)$ Å
$b = 5.5717\,(2)$ Å
$c = 25.6759\,(11)$ Å
$\beta = 128.311\,(3)°$
$V = 2215.60\,(17)$ Å^3
$Z = 2$
$D_x = 1.357$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5045 reflections
$\theta = 4.18–27.48°$
$\mu = 0.177$ mm^{-1}
$T = 100.0\,(1)$ K
Block
0.30 × 0.25 × 0.23 mm
Colourless

Data collection

KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{min} = 0.949$, $T_{max} = 0.960$
22 794 measured reflections
5045 independent reflections

3338 reflections with $I > 2\sigma(I)$
$R_{int} = 0.070$
$\theta_{max} = 27.48°$
$h = 0 \rightarrow 25$
$k = -7 \rightarrow 0$
$l = -33 \rightarrow 25$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.102$
$S = 0.956$
5045 reflections
300 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.198$ e Å^{-3}
$\Delta\rho_{min} = -0.297$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—C11	1.782 (2)	N31—C36	1.338 (2)
S1—C21	1.783 (2)	N41—C42	1.342 (2)
O14—C14	1.363 (2)	N41—C46	1.339 (2)
O24—C24	1.354 (2)	N51—C52	1.340 (2)
N31—C32	1.333 (2)	N51—C56	1.339 (2)
C11—S1—C21	102.38 (7)	O24—C24—C23	122.8 (2)
O14—C14—C13	117.7 (1)	C32—N31—C36	116.0 (2)
O14—C14—C15	122.7 (1)	C42—N41—C46	116.7 (2)
O24—C24—C25	117.9 (1)	C52—N51—C56	115.7 (2)
C21—S1—C11—C12	−57.2 (2)	C11—S1—C21—C22	−90.0 (1)
C21—S1—C11—C16	125.3 (1)	C11—S1—C21—C26	92.6 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H14···N31	0.84	1.92	2.736 (2)	162
O24—H24···N41	0.84	1.85	2.683 (2)	169

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ from the systematic absences. H atoms were treated as riding atoms with C—H = 0.95 and O—H = 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1999). Software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1306). Services for accessing these data are described at the back of the journal.

References

Bényei, A. C., Coupar, P. I., Ferguson, G., Glidewell, C., Lough, A. J. & Meehan, P. R. (1998). *Acta Cryst.* C**54**, 1515–1519.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996*a*). *Acta Cryst.* C**52**, 2524–2528.

Coupar, P. I., Ferguson, G. & Glidewell, C. (1996*b*). *Acta Cryst.* C**52**, 3055–3057.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Ferguson, G. (1999). *PRPKAPPA. A WordPerfect*-5.1 *Macro to Formulate and Polish CIF Format Files from the SHELXL*97 *Refinement of KappaCCD Data*. University of Guelph, Canada.

Ferguson, G., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 513–520.

Ferguson, G., Glidewell, C., Gregson, R. M. & Lavender, E. S. (1999). *Acta Cryst.* B**55**, 573–590.

Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 129–138.

Ferguson, G., Glidewell, C. & Lavender, E. S. (1999). *Acta Cryst.* B**55**, 591–600.

Glidewell, C., Ferguson, G., Lough, A. J. & Zakaria, C. M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1971–1982.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lavender, E. S., Ferguson, G. & Glidewell, C. (1999). *Acta Cryst.* C**55**, 430–432.

Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Sheldrick, G. M. (1997*a*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON. Molecular Geometry and Graphics Program*. Version of January 1999. University of Utrecht, The Netherlands.

Wheatley, P. S., Lough, A. J., Ferguson, G. & Glidewell, C. (1999). *Acta Cryst.* C**55**, 1489–1492.

Acta Cryst. (1999). C**55**, 1892–1896

Self-templating of large rings by small rings in 4,4′-bipyridyl-3,4-dihydroxy-3-cyclobutene-1,2-dione (2/3)

ELIZABETH J. MACLEAN,[a] PAUL S. WHEATLEY,[b] GEORGE FERGUSON[b]† AND CHRISTOPHER GLIDEWELL[b]

[a]*CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England, and* [b]*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland. E-mail: cg@st-andrews.ac.uk*

(*Received 6 July 1999; accepted 12 July 1999*)

Abstract

The title compound is a salt, bis(4,4′-bipyridyl-4,4′-diium) bis[3,4-dihydroxy-3-cyclobutene-1,2-dionate(1−)] 3,4-dihydroxy-3-cyclobutene-1,2-dionate(2−), $2C_{10}H_{10}N_2^{2+} \cdot 2C_4HO_4^- \cdot C_4O_4^{2-}$. The cations and the $(C_4O_4)^{2-}$ anions are linked by two types of short N—H···O hydrogen bond [N···O 2.595 (2) and 2.622 (2) Å; N—H···O 167 and 170°] to form a planar rectangular net built from a single type of centrosymmetric $R_8^6(56)$ ring. The $(C_4HO_4)^-$ anions are linked by paired short O—H···O hydrogen bonds [O···O 2.471 (2) Å and O—H···O 152°] into centrosymmetric dimers containing an

---

† On leave from the Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Acta Crystallographica Section C
ISSN 0108-2701 © 1999