

1985). Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* (Version of January 1994).

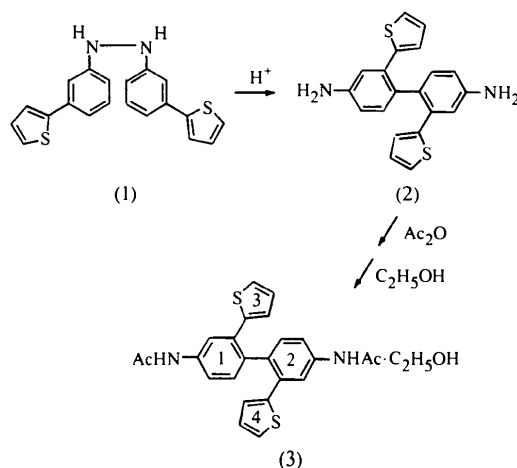
Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1276). Services for accessing these data are described at the back of the journal.

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## Comment

4,4'-Diamino-2,2'-di(2-thienyl)biphenyl, (2), was isolated from the acid-catalyzed benzidine rearrangement (Subotkowski, K.-Subotkowska & Shine, 1993) of bis-[3-(2-thienyl)phenyl]diazane, (1). Acetylation of compound (2), followed by recrystallization from ethanol gave the title compound, (3). Work-up and characterization details of compounds (1)–(3) will be published elsewhere. The <sup>1</sup>H NMR spectra showed that the chemical shift of H9 and H9' present in the thienyl rings of compound (3) was 6.53 p.p.m., *i.e.* shifted unusually upfield, suggesting that these two H atoms are oriented towards shielded regions of the phenyl rings. The molecular structure of compound (3) has been investigated to clarify the molecular conformation of the ring systems.



Bond lengths and angles for the molecule are as expected. The O1—C11 [1.218(5) Å] and O1'—C11' [1.228(5) Å] bond lengths of the acetylamino groups correspond to double bonds (Table 1). In the thienyl rings, the S—C distances range from 1.633(4) to 1.716(4) Å, with an average value of 1.688(3) Å; the two C—S—C angles are 93.1(3) and 93.1(2)°, with an average value of 93.1(2)°. These values are similar to those found for 2-(2-aminophenylthio)-2-(2-thienyl)ethyl 2-thienyl ketone (Morgant, Labouze, Viossat, Lancelot & Dung, 1996).

Each of the four aromatic rings in the title molecule is planar, with a maximum deviation of 0.017(3) Å for the C1 atom of the C1–C6 phenyl ring. The dihedral angle between the two phenyl rings is 63.7(1)° and those between the phenyl rings and the connected thienyl rings are 37.8(2) and 39.9(1)°.

The distances between H9 and H9' and the C atoms in the primed and unprimed phenyl rings are in the ranges 2.834(6)–3.957(7) and 2.790(5)–3.809(6) Å, respectively, and the distances between H9 and H9' and the centroids of the primed and unprimed phenyl rings are 3.153(5) and 3.052(4) Å. These distances reveal that H9 and H9' are positioned above the primed and

*Acta Cryst.* (1997). **C53**, 1320–1322

## 4,4'-Bis(acetylamino)-2,2'-di(2-thienyl)biphenyl-Ethanol (1/1)

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(Received 3 December 1996; accepted 24 April 1997)

## Abstract

Dihedral angles between the four aromatic rings in the title compound, C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>.C<sub>2</sub>H<sub>5</sub>OH, show that the rings are twisted relative to each other, with H atoms oriented towards shielded phenyl ring regions. Hydrogen bonding between the biphenyl molecule and the solvent ethanol connect these units in infinite layers.

unprimed phenyl rings, respectively, causing H9 and H9' signals to be shifted upfield in the NMR spectrum, as observed.

There is one intramolecular hydrogen bond between the O1' atom in the acetylamino group and the O atom in the solvent ethanol molecule, and two intermolecular hydrogen bonds by N and N' atoms arranging the molecules in layers parallel to  $[\bar{1}10]$ .

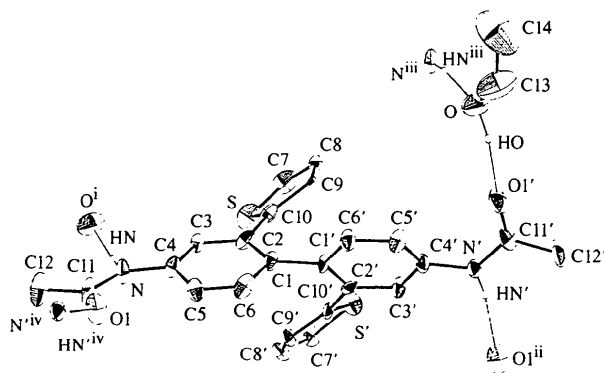


Fig. 1. ORTEP (Johnson, 1976) drawing of the title molecule showing the atom-labelling scheme. The displacement ellipsoids are drawn at the 40% probability level and H atoms are drawn as small circles of arbitrary radii. Hydrogen bonds are indicated by thin lines. Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $-x, \frac{1}{2}+y, -\frac{1}{2}-z$ ; (iii)  $-x, 1-y, -z$ ; (iv)  $-x, -\frac{1}{2}+y, -\frac{1}{2}+z$ .

## Experimental

Acid-catalyzed benzidine rearrangement of bis[3-(2-thienyl)phenyl]diazane (1), was carried out by following the general procedure of Subotkowski, K.-Subotkowska & Shine (1993). Biphenyl derivative (2) was acetylated and recrystallized from aqueous ethanol to afford 4,4'-bis(acetylamino)-2,2'-di(2-thienyl)biphenyl-ethanol (1/1), (3).

### Crystal data

$C_{24}H_{20}N_2O_2S_2 \cdot C_2H_6O$   
 $M_r = 478.61$   
 Monoclinic  
 $P2_1/c$   
 $a = 13.228 (3) \text{ \AA}$   
 $b = 12.805 (2) \text{ \AA}$   
 $c = 16.817 (6) \text{ \AA}$   
 $\beta = 119.35 (2)^\circ$   
 $V = 2482.9 (11) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.280 \text{ Mg m}^{-3}$   
 $D_m$  not measured

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: none

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 25  
 reflections  
 $\theta = 19.89\text{--}25.21^\circ$   
 $\mu = 0.244 \text{ mm}^{-1}$   
 $T = 288 (2) \text{ K}$   
 Parallelepiped  
 $0.26 \times 0.23 \times 0.07 \text{ mm}$   
 Colorless

$\theta_{\max} = 25.97^\circ$   
 $h = -16 \rightarrow 14$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 20$

4869 measured reflections  
 4869 independent reflections  
 1476 reflections with  
 $I > 2\sigma(I)$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.121$   
 $S = 0.737$   
 4869 reflections  
 298 parameters  
 Only coordinates of H atoms  
 refined

3 standard reflections  
 frequency: 240 min  
 intensity decay: 1.67%

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.5P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.307 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.325 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}, ^\circ$ )

S—C7	1.633 (4)	S'—C7'	1.704 (4)
S—C10	1.700 (4)	S'—C10'	1.716 (4)
O1—C11	1.218 (5)	O1'—C11'	1.228 (5)
C7—C8	1.338 (6)	C7'—C8'	1.340 (5)
C8—C9	1.449 (5)	C8'—C9'	1.424 (5)
C9—C10	1.465 (5)	C9'—C10'	1.388 (5)
C7—S—C10	93.1 (3)	C8—C9—C10	106.6 (3)
C8—C7—S	114.8 (4)	C2—C10—S	118.0 (3)
C7—C8—C9	114.0 (4)		

Table 2. Hydrogen-bonding geometry ( $\text{\AA}, ^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O—HO...O1'	0.819 (7)	1.943 (6)	2.726 (6)	159.8 (5)
N—HN...O'	0.861 (6)	2.025 (7)	2.881 (7)	172.6 (5)
N'—HN'...O1''	0.860 (6)	2.024 (5)	2.873 (5)	169.0 (4)

Symmetry codes: (i)  $-x, 1-y, -z$ ; (ii)  $-x, \frac{1}{2}+y, -\frac{1}{2}-z$ .

Data collection of only an asymmetric unit (Suh *et al.*, 1993), cell refinement and data reduction were carried out using *SDP-Plus* (Frenz, 1985). The structure was solved by direct methods using *SHELX86* (Sheldrick, 1985). Refinement was performed with *SHELXL93* (Sheldrick, 1993) using anisotropic displacement parameters for all non-H atoms. H atoms were included at calculated positions and refined with fixed isotropic displacement parameters of  $0.05 \text{ \AA}^2$ . Molecular graphics were prepared using *ORTEP* (Johnson, 1976) and the material for publication using *SHELXL93*.

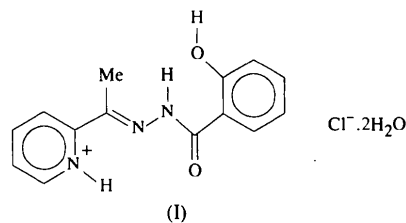
KHP acknowledges KOSEF-OCRC (1996) and the Ministry of Education through the Basic Science Research Institute Program (BSRI-96-3433) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1451). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1997). **C53**, 1322–1323

## 2-[1-(Salicyloylhydrazone)ethyl]pyridinium Chloride Dihydrate at 173 K

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(Received 27 January 1997; accepted 25 March 1997)

### Abstract

The approximately planar molecule of the title compound, C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup>·Cl<sup>-</sup>·2H<sub>2</sub>O, is in an *E* conformation with respect to the C=N bond, with a C—C=N—N torsion angle of 179.5(1)°. The maximum possible number of hydrogen bonds are formed in the crystal. The pyridinium H atom forms a hydrogen bond to a water molecule which is hydrogen bonded to the carbonyl O atom, requiring the pyridine ring to be rotated 180° compared to the unprotonated 2-formylpyridine analog. There is an intramolecular hydrogen bond involving the NH group on the chain and the hydroxyl O atom on the phenyl ring which, in turn, is hydrogen bonded to a Cl<sup>-</sup> ion. Finally, a water molecule and chloride ion form a hydrogen-bonded square around a center of symmetry, with O···Cl distances of 3.199(2) and 3.206(2) Å, and endocyclic angles of 91.17(4) and 88.83(4)° at the O and Cl atoms, respectively.

### Comment

Although Schiff base complexes of salicylaldehyde have been extensively studied, there are few reports utilizing the related salicyloylhydrazide. As part of a program which uses tridentate ligands to complex various metal ions, we synthesized 2-acetylpyridine salicyloylhydrazone. In the course of our studies, we isolated colorless crystals of the chloride salt dihydrate of the protonated ligand, (I). The structure was determined to establish the conformation of the protonated species for comparison with the related 2-formylpyridine salicyloylhydrazone reported by Domiano, Musatti, Pelizzi & Predieri (1974) (henceforth DMPP).

The cation shown in Fig. 1 can be viewed as an approximately planar molecule consisting of three planar segments: the pyridine ring, the hydroxybenzene ring and the hydrazone link between the two rings. Relative to the plane of the pyridine ring (N1, C1–C5), the remaining atoms, with the exception of C6', all lie on one side. The deviations include a twist of 4.03(8)° of the chain C6=N2–N3–C7(=O1)—C8, with respect to the pyridine ring. The chain is also twisted by 1.75(9)° relative to the benzene ring (C8–C13). The twists and distortions in our protonated form are all slightly less than in the unprotonated form reported by DMPP. The hydrogen bonding shown in Fig. 2,

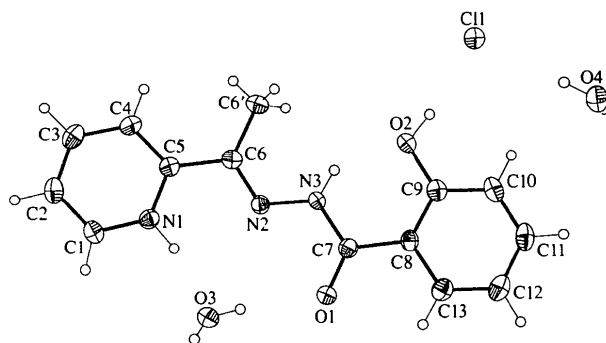


Fig. 1. The molecular structure of (I) with 50% probability ellipsoids and the atom-numbering scheme.

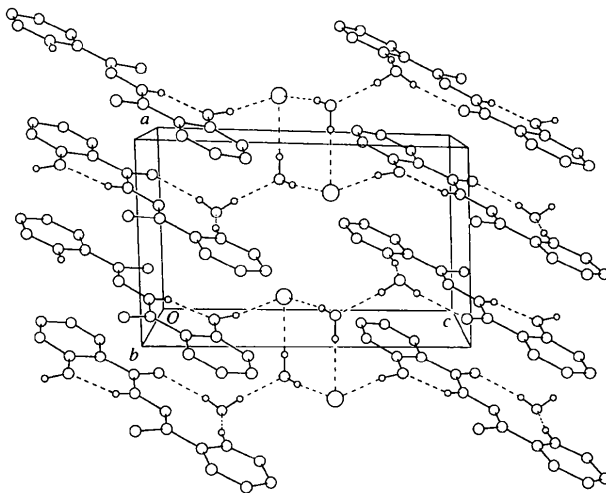


Fig. 2. View of the packing of (I) in the *ab* plane.