| | | | |
|---|---|---|---|
| N2 | 0.7371 (2) | 0.3820 (2) | 0.3688 (4) | 0.0512 (14) |
| N1 | 0.8337 (2) | 0.3716 (3) | 0.3570 (4) | 0.0568 (15) |
| C3 | 0.5845 (3) | 0.2969 (2) | 0.2128 (6) | 0.0431 (19) |
| C2 | 0.6596 (3) | 0.3814 (3) | 0.2030 (6) | 0.0421 (18) |
| C9 | 0.4841 (3) | 0.4262 (2) | 0.2746 (5) | 0.0397 (19) |
| C1 | 0.5816 (4) | 0.4634 (2) | 0.2185 (6) | 0.0474 (22) |
| C4 | 0.4854 (3) | 0.3297 (3) | 0.2692 (5) | 0.0398 (20) |
| C4' | 1.0580 (3) | 0.3744 (3) | 0.8147 (7) | 0.0550 (22) |
| C1' | 0.9064 (3) | 0.3713 (3) | 0.5187 (7) | 0.0464 (25) |
| C7 | 0.3191 (4) | 0.4225 (3) | 0.3785 (6) | 0.0578 (22) |
| C8 | 0.4000 (4) | 0.4742 (3) | 0.3290 (6) | 0.0497 (21) |
| C6 | 0.3202 (4) | 0.3259 (3) | 0.3721 (7) | 0.0595 (24) |
| C5 | 0.4022 (4) | 0.2780 (3) | 0.3175 (6) | 0.0495 (20) |
| C10 | 0.7077 (4) | 0.3827 (3) | 0.0479 (7) | 0.0612 (25) |
| C6' | 0.8727 (3) | 0.3651 (3) | 0.6692 (7) | 0.0540 (25) |
| C3' | 1.0929 (3) | 0.3783 (4) | 0.6654 (8) | 0.0694 (25) |
| C2' | 1.0175 (3) | 0.3763 (4) | 0.5168 (7) | 0.0671 (23) |
| C5' | 0.9476 (3) | 0.3662 (4) | 0.8195 (6) | 0.0599 (21) |

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

| | | | |
|---|---|---|---|
| C1—C4' | 1.733 (5) | C9—C8 | 1.393 (6) |
| O1—C3 | 1.209 (4) | C4—C5 | 1.389 (6) |
| O2—C1 | 1.208 (4) | C4'—C3' | 1.360 (5) |
| N2—N1 | 1.231 (4) | C4'—C5' | 1.385 (5) |
| N2—C2 | 1.494 (4) | C1'—C6' | 1.364 (5) |
| N1—C1' | 1.440 (5) | C1'—C2' | 1.385 (5) |
| C3—C2 | 1.545 (5) | C7—C8 | 1.371 (6) |
| C3—C4 | 1.471 (6) | C7—C6 | 1.392 (5) |
| C2—C1 | 1.548 (6) | C6—C5 | 1.372 (6) |
| C2—C10 | 1.489 (6) | C6'—C5' | 1.382 (5) |
| C9—C1 | 1.474 (6) | C3'—C2' | 1.375 (6) |
| C9—C4 | 1.391 (4) | | |
| N1—N2—C2 | 113.5 (3) | C1—C9—C8 | 128.9 (3) |
| N2—N1—C1' | 112.4 (3) | C1—C9—C4 | 109.8 (3) |
| O1—C3—C4 | 127.6 (3) | C2—C1—C9 | 108.2 (3) |
| O1—C3—C2 | 124.2 (3) | O2—C1—C9 | 127.6 (3) |
| C2—C3—C4 | 108.2 (3) | O2—C1—C2 | 124.2 (4) |
| N2—C2—C3 | 104.5 (3) | C3—C4—C9 | 110.3 (3) |
| C3—C2—C10 | 113.4 (4) | C9—C4—C5 | 120.9 (4) |
| C3—C2—C1 | 101.7 (3) | C3—C4—C5 | 128.9 (4) |
| N2—C2—C10 | 117.6 (4) | C1—C4'—C5' | 118.8 (4) |
| N2—C2—C1 | 103.2 (3) | C1—C4'—C3' | 120.2 (3) |
| C1—C2—C10 | 114.7 (4) | C3'—C4'—C5' | 120.9 (5) |
| C4—C9—C8 | 121.3 (3) | N1—C1'—C2' | 116.3 (5) |
| N1—C1'—C6' | 124.3 (4) | C4—C5—C6 | 117.4 (4) |
| C6'—C1'—C2' | 119.4 (5) | C1'—C6'—C5' | 120.9 (4) |
| C8—C7—C6 | 121.3 (5) | C4'—C3'—C2' | 119.7 (4) |
| C9—C8—C7 | 117.3 (4) | C1'—C2'—C3' | 120.3 (4) |
| C7—C6—C5 | 121.8 (4) | C4'—C5'—C6' | 118.7 (4) |

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71376 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1072]

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# Structure of 3-Benzyl-2-(3-hydroxy-2-pyridylimino)-4-methyl-2,3-dihydro-1,3-thiazole,† C16H15N3OS

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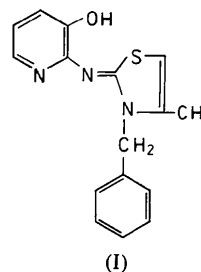
## Abstract

The hydroxyl H atom takes part in a bifurcated hydrogen bond. The strong intramolecular $O—H \cdots N_{imino}$ bond is complemented by the weak $O—H \cdots O$ bond [$O \cdots O$ 3.023 (3), $H \cdots O$ 2.58 (3) Å, $O—H \cdots O$ 113 (2)°], which is responsible for the coupling of the molecules in centrosymmetric dimers. The bifurcation angle $N \cdots H \cdots O$ is 100 (1)°. The molecular dimers are held together only by van der Waals forces.

## Comment

The synthetic route for functionalized thiadiazines and thiazolimines was reported recently by Tosheva & Kalcheva (1993). Ring transformations of oxazoles into analogous derivatives have been discussed previously (Sasaki, Ito & Shimizu, 1982).



(I)

In the title compound (I), the thiazole ring is planar to within 0.004 (3) Å and the interatomic distances in the ring indicate double-bond character for C2—C3 [1.332 (5) Å]. The lengths of S—C1 [1.762 (4) Å] and S—C3 [1.749 (3) Å] fall within the range of an $S—C_{sp^2}$ single bond [1.751 (17) Å; Allen *et al.*, 1987]. The C1—

† 2-(3-Benzyl-4-methyl-2,3-dihydro-1,3-thiazol-2-ylideneamino)-pyridin-2-ol.

S—C3 angle is 90.3 (2)°. The exocyclic C1—N2 bond [1.297 (4) Å] is short enough to be a double bond and the N2—C1a distance [1.383 (3) Å] is shorter than the calculated mean $C_{ar}$—N(2) value of 1.431 (20) Å (Allen *et al.*, 1987). The phenyl and hydroxypyridyl rings are tilted with respect to the thiazole ring by 97.8 (1) and 5.6 (7)°, respectively.

The title compound has similar molecular geometry to 3N-benzyl-2-(2-hydroxyphenylimino)-4-methyl-2,3(2H)-thiazole (BHMT) (Kalcheva, Tosheva & Hadjieva, 1993). The optimal superposition (Diamond, 1988) of the two molecules (ten non-H atoms, excluding most atoms of the side rings) results in the overall residual *s* = 0.019 (Chernikova, Lavut & Zorkii, 1979) and the maximum distance between equivalent atoms $R_{max}$ = 0.093 Å for C1a. Their molecular conformations differ in the rotations of the phenyl rings around the C1b—C4 bond, calculated as a dihedral angle between the ring plane and the N1—C4—C1b plane [51.8 (2) and 28.4 (3)°], and the hydroxypyridyl (hydroxyphenyl in BHMT) ring around the C1a—N2 bond referred to as the C1—N2—C1a plane [5 (2) and 22.6 (4)° for the title compound and BHMT, respectively].
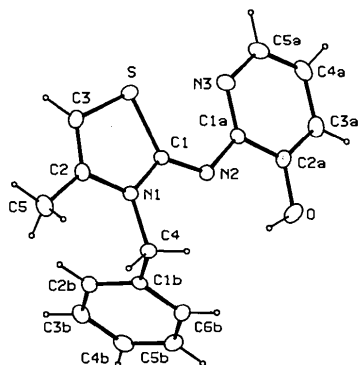


Fig. 1. A view of the molecule with the atom-numbering scheme and 20% probability thermal ellipsoids; H-atom spheres are arbitrarily reduced.
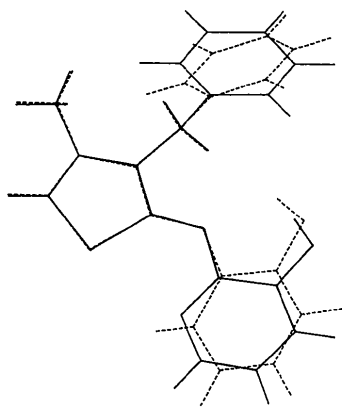


Fig. 2. A superposition of the title molecule (solid lines) and BHMT (dashed lines) (Kalcheva *et al.*, 1993).

## Experimental

### Crystal data

$C_{16}H_{15}N_3OS$
$M_r$ = 297.38
Triclinic
$P\bar{1}$
*a* = 8.428 (2) Å
*b* = 9.816 (2) Å
*c* = 10.064 (2) Å
$\alpha$ = 64.55 (2)°
$\beta$ = 73.66 (2)°
$\gamma$ = 79.39 (2)°
*V* = 719.5 (3) Å$^3$
*Z* = 2

$D_x$ = 1.372 Mg m$^{-3}$
Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 24 reflections
$\theta$ = 19.01–19.76°
$\mu$ = 0.21 mm$^{-1}$
*T* = 292 K
Prismatic
0.34 × 0.27 × 0.10 mm
Colourless

### Data collection

Enraf-Nonius CAD-4 diffractometer
Continuous scan profiles
Absorption correction: none
3659 measured reflections
2522 independent reflections
1660 observed reflections
[$I > 3.0\sigma(I)$]

$R_{int}$ = 0.021
$\theta_{max}$ = 25°
*h* = −10 → 10
*k* = −11 → 11
*l* = −11 → 11
3 standard reflections frequency: 120 min intensity variation: 0.9%

### Refinement

Refinement on *F*
*R* = 0.042
*wR* = 0.040
*S* = 1.774
1660 reflections
193 parameters
H atoms refined as riding atoms

$w = 1/[\sigma^2(F) + (0.001F)^2]$
$(\Delta/\sigma)_{max}$ = 0.065
$\Delta\rho_{max}$ = 0.218 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.294 e Å$^{-3}$
Atomic scattering factors from *SDP/PDP* (Enraf-Nonius, 1985)

The hydroxyl H atom was localized from a $\Delta\rho$ map, the other H-atom positions were calculated. The hydroxyl H atom was refined with a fixed isotropic thermal factor and the rest of the H atoms were refined as riding atoms. Data collection: *CAD*-4 (Enraf-Nonius, 1988). Data reduction: *SDP/PDP* (Enraf-Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP/PDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992).

Table 1. *Positional and equivalent isotropic displacement parameters* (Å$^2$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S | 0.8211 (1) | 0.43694 (8) | 0.50835 (8) | 0.0395 (2) |
| O | 0.6794 (3) | −0.0595 (2) | 0.4942 (2) | 0.0585 (8) |
| N1 | 0.6360 (3) | 0.4738 (2) | 0.3311 (2) | 0.0321 (7) |
| N2 | 0.6997 (3) | 0.2188 (2) | 0.4651 (2) | 0.0334 (7) |
| N3 | 0.8612 (3) | 0.1268 (3) | 0.6510 (2) | 0.0434 (8) |
| C1 | 0.7121 (4) | 0.3595 (3) | 0.4344 (3) | 0.0308 (9) |
| C2 | 0.6608 (4) | 0.6204 (3) | 0.3085 (3) | 0.037 (1) |
| C3 | 0.7569 (4) | 0.6197 (3) | 0.3936 (3) | 0.041 (1) |
| C4 | 0.5393 (4) | 0.4365 (3) | 0.2516 (3) | 0.0363 (9) |
| C5 | 0.5838 (5) | 0.7574 (3) | 0.2008 (3) | 0.055 (1) |
| C1a | 0.7786 (4) | 0.1037 (3) | 0.5690 (3) | 0.0327 (9) |
| C2a | 0.7664 (4) | −0.0429 (3) | 0.5812 (3) | 0.039 (1) |

| | | | |
|---|---|---|---|
| C3a | 0.8420 (4) | −0.1649 (3) | 0.6784 (3) | 0.048 (1) |
| C4a | 0.9295 (4) | −0.1401 (3) | 0.7635 (3) | 0.051 (1) |
| C5a | 0.9348 (4) | 0.0046 (3) | 0.7470 (3) | 0.050 (1) |
| C1b | 0.6486 (3) | 0.3854 (3) | 0.1309 (3) | 0.0314 (9) |
| C2b | 0.7729 (4) | 0.4708 (3) | 0.0206 (3) | 0.039 (1) |
| C3b | 0.8705 (4) | 0.4245 (3) | −0.0904 (3) | 0.045 (1) |
| C4b | 0.8437 (4) | 0.2914 (3) | −0.0927 (3) | 0.049 (1) |
| C5b | 0.7195 (4) | 0.2056 (3) | 0.0160 (3) | 0.051 (1) |
| C6b | 0.6217 (4) | 0.2515 (3) | 0.1277 (3) | 0.043 (1) |

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

| | | | |
|---|---|---|---|
| S—C1 | 1.762 (4) | N3—C5a | 1.350 (4) |
| S—C3 | 1.749 (3) | C2—C3 | 1.332 (5) |
| O—C2a | 1.364 (5) | C2—C5 | 1.492 (4) |
| N1—C1 | 1.363 (3) | C4—C1b | 1.516 (4) |
| N1—C2 | 1.404 (4) | C1a—C2a | 1.412 (5) |
| N1—C4 | 1.471 (5) | C2a—C3a | 1.363 (4) |
| N2—C1 | 1.297 (4) | C3a—C4a | 1.392 (6) |
| N2—C1a | 1.383 (3) | C4a—C5a | 1.366 (5) |
| N3—C1a | 1.327 (5) | | |
| C1—S—C3 | 90.3 (2) | S—C3—C2 | 112.8 (2) |
| C1—N1—C2 | 115.2 (3) | N1—C4—C1b | 112.4 (2) |
| C1—N1—C4 | 119.2 (2) | N2—C1a—N3 | 123.6 (3) |
| C2—N1—C4 | 125.5 (2) | N2—C1a—C2a | 114.8 (3) |
| C1—N2—C1a | 121.0 (3) | N3—C1a—C2a | 121.7 (2) |
| C1a—N3—C5a | 117.7 (3) | O—C2a—C1a | 118.9 (2) |
| S—C1—N1 | 109.3 (2) | O—C2a—C3a | 121.2 (3) |
| S—C1—N2 | 129.3 (2) | C1a—C2a—C3a | 119.9 (4) |
| N1—C1—N2 | 121.4 (3) | C2a—C3a—C4a | 118.3 (3) |
| N1—C2—C3 | 112.3 (2) | C3a—C4a—C5a | 118.7 (3) |
| N1—C2—C5 | 121.7 (3) | N3—C5a—C4a | 123.8 (4) |
| C3—C2—C5 | 126.0 (3) | | |
| C1—N1—C4—C1b | −74.8 (3) | C1—N2—C1a—C2a | −174.6 (3) |
| C2—N1—C4—C1b | 104.0 (3) | N1—C4—C1b—C2b | −52.7 (4) |
| C1a—N2—C1—S | −0.1 (4) | N1—C4—C1b—C6b | 129.0 (3) |
| C1a—N2—C1—N1 | 179.4 (3) | N2—C1a—C2a—O | −0.7 (4) |
| C1—N2—C1a—N3 | 4.8 (4) | | |

A mixture of 2-(2-oxopropylthio)oxazolo[4,5-b]pyridine, benzylamine and perchloric acid was warmed at 313 K for 1h. After neutralization with HCl it was left in a cool place overnight. The product was filtered, dried and recrystallized from EtOH/H₂O (2:1).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71406 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1049]

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# Structures of 1,1-Diphenyl-2-aza-1,3-butadienes. IV. 3-Cyano-4-(2,4-dichlorophenyl)-1,1-diphenyl-2-aza-1,3-butadiene (24CLPD) and 3-Cyano-4-(2,4-dimethoxyphenyl)-1,1-diphenyl-2-aza-1,3-butadiene (24MOPD)

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## Abstract

The 2,4-disubstituted derivatives [24CLPD: 3-(2,4-dichlorophenyl)-2-(diphenylmethyleneamino)propenonitrile, $C_{22}H_{14}Cl_2N_2$; 24MOPD: 3-(2,4-dimethoxyphenyl)-2-(diphenylmethyleneamino)propenonitrile, $C_{24}H_{20}N_2O_2$] have the Z configuration, as in the previously described monosubstituted representatives from this series. The C1c—C3 bond length [in Phc—C3=C2(CN)—N1=C1(Pha)(Phb)] is 1.459 (5) Å in 24CLPD, which is slightly longer than in 24MOPD, 1.448 (3) Å, while the C3—C2 bond in 24CLPD, 1.337 (5) Å, is shorter than in 24MOPD, 1.357 (4) Å. The c ring is twisted out of the C1c—C3=C2(N1)—C4 plane by 10.9 (2) and 21.8 (2)° for 24CLPD and 24MOPD, respectively. The C1=N1—C2—C3 torsion angle in 24MOPD, 151.6 (3)°, is the largest among those determined so far. In 24CLPD, this angle has the mean value 135.9 (3)°. The dihedral angles between the N1=C1(C1a)—C1b plane and the a and b phenyl rings are 15.0 (1)/20.4 (3) and 58.3 (1)/62.3 (1)° for 24CLPD/24MOPD, respectively. Correspondingly, the C1a—C1 bond distances, 1.481 (4)/1.488 (5) Å, are shorter than C1b—C1, 1.488 (4)/1.490 (3) Å. The molecules are held together only by dispersion forces and both compounds obey the close-