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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···Br1	0.95	2.69	3.639 (9)	173.5
C14—H14···Br1^{i}	0.95	2.91	3.857 (10)	173.1
C24—H24···Br1^{ii}	0.95	2.75	3.673 (8)	163.0
C12—H12···Br1^{iii}	0.95	2.81	3.704 (10)	156.8
C22—H22···Br2	0.95	2.90	3.768 (8)	153.2
C15—H15···Br2^{iv}	0.95	2.84	3.711 (10)	152.6

Symmetry codes: (i) $x, y, 1 + z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, z$; (iv) $1 - x, 1 - y, \frac{1}{2} + z$.

The data collection nominally covered over a sphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 6.0 cm. Coverage of the unique set is over 96% complete to at least 25° in θ, regarding Friedel opposites as distinct. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. All H atoms could be located by difference Fourier synthesis and were refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ or $U(\text{H}) = 1.2\ U_{\text{eq}}(\text{C})$], using a riding model with methyl C—H = 0.98, aromatic C—H = 0.95 or secondary C—H = 0.99 Å. The methyl groups were allowed to rotate about their local threefold axis. The final electron-density map shows one peak of 3.124 eÅ^{-3} at a distance of 0.97 Å from Br2, probably attributable to residual absorption errors. The crystal was a racemic twin, and the ratio of the twin components refined to 0.58 (2):0.42(2).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1295). Services for accessing these data are described at the back of the journal.

References

Ackermann, J., Tacke, R., Wannagat, U., Koke, U. & Meyer, F. (1980). *Arch. Pharm.* **313**, 129–141.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Burger, H., Hensen, K. & Pickel, P. (1995). *Z. Anorg. Allg. Chem.* **621**, 101–104.

Engelhardt, U. & Rosefid, M. (1994). *Z. Anorg. Allg. Chem.* **620**, 620–624.

Hensen, K., Gebhardt, F. & Bolte, M. (1997). *Z. Anorg. Allg. Chem.* **623**, 633–636.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1995). *SMART and SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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3-[(2-Bromo-4-methylphenyl)iminomethyl]-2-hydroxy-5-methylbenzaldehyde

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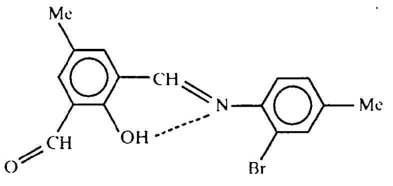
Abstract

Molecules of the title compound, $C_{16}H_{14}BrNO_2$, are almost planar. Each contains a strong intramolecular N···H—O hydrogen bond between the imine and hydroxyl groups [N···O 2.574 (5) Å].

Comment

Schiff base compounds can be classified by their photochromic and thermochromic characteristics in the solid state by proton transfer from the hydroxyl O atom to the imine N atom (Cohen *et al.*, 1964). The charge transport occurs through overlapping intramolecular π orbitals with proton transfer (Hadjoudis *et al.*, 1987). Proton transfer could also provide the basis for molecular switches (Xu *et al.*, 1994). In the course of a systematic structural investigation of Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997; Elerman, Kabak, Elmali & Svoboda, 1998; Elerman & Elmali, 1998; Elerman, Elmali, Svoboda & Fuess, 1998; Elmali *et al.*, 1995; Elmali & Elerman, 1997, 1998; Elmali, Elerman & Zeyrek, 1998; Elmali, Elerman & Kendi, 1998), the structure of the title compound, (I), was determined.



(I)

From some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromic properties are planar, while those exhibiting photochromic properties are non-planar (Moustakali-Mavridis *et al.*, 1978). In agreement with the conclusions above, the title molecule is ther-

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mochromic (Elmali, 1998) and almost planar; moieties *A* (C1–C7, Br1, N1) and *B* (C8–C16, O1, O2) [both planar with a maximum deviation of 0.025 (4) Å for C1] are inclined at an angle of 5.4 (2)°. It was concluded that in Schiff base compounds, planarity of the molecule makes it possible for the proton to transfer through the hydrogen bond in the ground state with a small energy requirement (Bregman, Leiserowitz & Schmidt, 1964; Bregman, Leiserowitz & Osaki, 1964).

Two types of intramolecular hydrogen bonds (N—H···O or N···H—O) can exist in Schiff bases (Garnovskii *et al.*, 1993). In (I), the O1···N1 distance of 2.574 (5) Å is clearly indicative of strong intramolecular hydrogen bonding; this distance is significantly shorter than the sum of the van der Waals radii for nitrogen and oxygen (3.07 Å; Bondi, 1964). The O1—C14 bond distance of 1.332 (5) Å is consistent with an O—C single bond; similarly, the N1—C8 distance of 1.264 (6) Å is consistent with a C═N double bond. Clearly, the enolimine tautomer is favoured over the ketamine form, and the intramolecular hydrogen-bond type is N···H—O. In the present study, the N1···O1 distance is comparable to that observed for thermochromic 2,2′-azinodimethyldiphenol [2.611 (6) Å; Xu *et al.*, 1994], for *N*,*N*′-disalicylidene-1,6-pyrenediamine [2.614 (5) Å; Inabe *et al.*, 1989], and also for 4-ethyl-2-(2-hydroxynaphthylmethylidene)amino-5-methyl-3-thiophenecarbonitrile [2.574 (3) Å; Elerman *et al.*, 1997].

Discrete monomeric molecules are held together in the crystal by van der Waals interactions. The molecules are stacked in columns along the *b* axis, with plane-to-plane separations of 3.351 (7) Å. The minimum distances between two non-H atoms in neighbouring molecules are C2···C5^i, C4···C8^i, C5···C9^i, C8···C10^i, C8···C11^i and C9···C12^i [symmetry code: (i) $x, y-1, z$], with values of 3.462 (7), 3.377 (8), 3.416 (6), 3.453 (8), 3.346 (7) and 3.375 (8) Å, respectively.

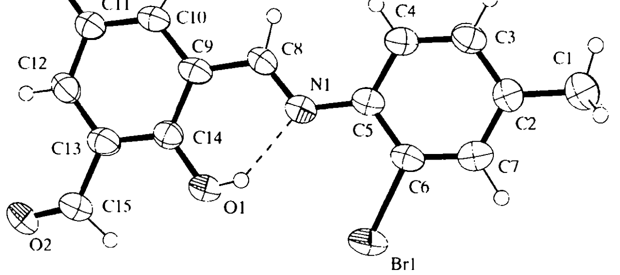

Fig. 1. The molecular structure and atomic labelling scheme of the title compound. Displacement ellipsoids are plotted at the 50% probability level (*ORTEP*II; Johnson, 1976).

Experimental

The title compound was obtained from the reaction of 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (0.0002 mol) with a solution of 2-bromo-4-methylaniline (0.0002 mol) in ethanol (15 ml). The precipitate which separated from the solution was recrystallized over a period of 24 h from acetonitrile solution.

Crystal data

$C_{16}H_{14}BrNO_2$
$M_r = 332.19$
Monoclinic
$P2_1/c$
$a = 19.735\,(3)$ Å
$b = 4.600\,(3)$ Å
$c = 15.654\,(2)$ Å
$\beta = 104.22\,(2)°$
$V = 1377.5\,(9)$ Å^3
$Z = 4$
$D_x = 1.602$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3.13–13.82°$
$\mu = 2.984$ mm^{-1}
$T = 303\,(2)$ K
Needle
0.55 × 0.08 × 0.05 mm
Orange

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.452$, $T_{max} = 0.861$
5143 measured reflections
2575 independent reflections

1323 reflections with $I > 2\sigma(I)$
$R_{int} = 0.130$
$\theta_{max} = 25.51°$
$h = -23 \rightarrow 23$
$k = -5 \rightarrow 0$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.098$
$S = 0.989$
2575 reflections
215 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2]$
where $P = F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.003$
$\Delta\rho_{max} = 0.400$ e Å^{-3}
$\Delta\rho_{min} = -0.366$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C5—N1	1.395 (6)	C14—O1	1.332 (5)
C6—Br1	1.902 (4)	O2—C15	1.183 (7)
C8—N1	1.264 (6)		
C6—C5—N1	118.9 (3)	O1—C14—C13	119.8 (3)
N1—C5—C4	125.6 (4)	O1—C14—C9	120.5 (4)
C7—C6—Br1	117.3 (3)	C8—N1—C5	123.0 (3)
C5—C6—Br1	119.3 (4)	O2—C15—C13	126.8 (5)
N1—C8—C9	121.4 (4)		

Diffraction intensities from the crystal were generally weak and only 52% of the reflections were observed with $I > 2\sigma(I)$, as evidenced by the high R_{int} value. The structure was solved by direct phase determination. The parameters of the complete structure could be refined by full-matrix anisotropic least squares. All phenyl rings were refined without any constraints. Values of distances and angles in the rings show no significant differences from those of an ideal benzene ring. All H-atom positions (except for the hydroxyl H1O atom) were calculated using a riding model and were considered with fixed isotropic *U* values in all refinements. The H1O atom was located in the difference Fourier maps calculated at the end of the refinement process as a small positive electron density and was not refined.

Data collection: *Nonius Diffractometer Control Software* (Nonius, 1993). Cell refinement: *Nonius Diffractometer Control Software*. Data reduction: *REDU*4 (Stoe & Cie, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1023). Services for accessing these data are described at the back of the journal.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bregman, J., Leiserowitz, L. & Osaki, K. (1964). *J. Chem. Soc.* pp. 2086–2100.
Bregman, J., Leiserowitz, L. & Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 2068–2085.
Cohen, M. D., Schmidt, G. M. J. & Flavian, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
Elerman, Y. & Elmali, A. (1998). *Acta Cryst.* C**54**, 529–531.
Elerman, Y., Elmali, A., Atakol, O. & Svoboda, I. (1995). *Acta Cryst.* C**51**, 2344–2346.
Elerman, Y., Elmali, A., Kabak, M., Aydin, M. & Peder, M. (1994). *J. Chem. Cryst.* **24**, 603–606.
Elerman, Y., Elmali, A., Kendi, E., Özbey, S. & Ertüzün, V. (1997). *Acta Cryst.* C**53**, 1158–1160.
Elerman, Y., Elmali, A., Svoboda, I. & Fuess, H. (1998). *Acta Cryst.* C**54**, 1076–1078.
Elerman, Y., Kabak, M., Elmali, A. & Svoboda, I. (1998). *Acta Cryst.* C**54**, 128–130.
Elerman, Y., Paulus, H., Svoboda, I. & Fuess, H. (1992). *Z. Kristallogr.* **198**, 135–136.
Elerman, Y., Svoboda, I. & Fuess, H. (1991). *Z. Kristallogr.* **196**, 309–311.
Elmali, A. (1998). Unpublished results.
Elmali, A. & Elerman, Y. (1997). *Acta Cryst.* C**53**, 791–793.
Elmali, A. & Elerman, Y. (1998). *J. Mol. Struct.* **442**, 31–37.
Elmali, A., Elerman, Y. & Kendi, E. (1998). *Acta Cryst.* C**54**, 1137–1139.
Elmali, A., Elerman, Y. & Zeyrek, C. T. (1998). *J. Mol. Struct.* **443**, 123–130.
Elmali, A., Özbey, S., Kendi, E., Kabak, M. & Elerman, Y. (1995). *Acta Cryst.* C**51**, 1878–1880.
Garnovskii, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–69.
Hadjoudis, E., Vitterakis, M. & Moustakali-Mavridis, I. (1987). *Tetrahedron*, **43**, 1345–1360.
Inabe, T., Hoshino, N., Mitani, T. & Maruyama, Y. (1989). *Bull. Chem. Soc. Jpn*, **42**, 2245–2251.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Moustakali-Mavridis, I., Hadjoudis, E. & Mavridis, A. (1978). *Acta Cryst.* B**34**, 3709–3715.
Nonius (1993). *Nonius Diffractometer Control Software*. Release 5.1. Nonius GmbH, Solingen, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Stoe & Cie (1991). *REDU4. Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
Xu, X., You, X., Sun, Z., Wang, X. & Liu, H. (1994). *Acta Cryst.* C**50**, 1169–1171.

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(1*RS*,10a*RS*)-3-Imino-1-(2-thienyl)-1,2,3,9,10,10a-hexahydrophenanthrene-2,2,4-tricarbonitrile

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Abstract

The title compound, $C_{21}H_{14}N_4S$, involves an exocyclic imino (C=NH) bond of 1.264 (3) Å. The relative stereochemistry at the two chiral centres is (*R*,*R*). The non-aromatic rings adopt half-chair conformations. The molecules are linked in centrosymmetric pairs by C=N—H···NC hydrogen bonds.

Comment

The highly reactive α,β-unsaturated nitriles have been extensively utilized in heterocyclic synthesis (Elgemeie, Elghandour, Elzanate & Hussein, 1997; Elgemeie, Elghandour, Ali & Hussein, 1997). We now report the novel reaction of 1,2,3,4-tetrahydro-1-naphthylidenemalononitrile, (1), with β-(2-thienylmethylidene)(cyano)acetamide, (2), to give a product identified as the unexpected phenanthrene, (5). The reaction is assumed to be initiated by an exchange process between the tetrahydronaphthylidene group of (1) and the thienylmethylidene group of (2), to give the intermediate (4), which then cyclizes *via* elimination of water to give (5). We also investigated the reaction between (1) and β-(2-thienylmethylidene)malononitrile, (6), under the same conditions. The product was identified as the same as