

Refinement

Refinement on F^2 $R(F) = 0.051$ $wR(F^2) = 0.122$ $S = 0.94$

1667 reflections

131 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = -0.001$ $\Delta\rho_{\max} = 0.11 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$

Extinction correction:

SHELXTL (Sheldrick, 1994)

Extinction coefficient:

0.000 (7)

Scattering factors from

International Tables for Crystallography (Vol. C)Table 1. Selected geometric parameters and hydrogen-bonding geometry (\AA , $^\circ$)

O1—C2	1.204 (4)	C2—C3	1.497 (5)	
O2—C9	1.197 (4)	C3—C4	1.536 (4)	
O3—C9	1.304 (4)	C4—C5	1.527 (6)	
C1—C10	1.508 (4)	C4—C7	1.548 (4)	
C1—C2	1.521 (4)	C5—C6	1.548 (6)	
C1—C6	1.536 (5)	C7—C9	1.515 (4)	
C1—C7	1.560 (4)	C7—C8	1.530 (4)	
C9—O3—H3	113 (3)	C3—C4—C7	102.3 (2)	
C2—C1—C6	102.4 (2)	C4—C5—C6	102.8 (3)	
C2—C1—C7	99.9 (2)	C1—C6—C5	104.6 (3)	
C6—C1—C7	101.7 (2)	C9—C7—C4	110.6 (3)	
O1—C2—C3	126.9 (3)	O9—C7—C1	116.3 (2)	
O1—C2—C1	125.2 (3)	C4—C7—C1	94.2 (2)	
C3—C2—C1	107.9 (2)	O2—C9—O3	122.3 (3)	
C2—C3—C4	101.7 (2)	O2—C9—C7	123.0 (3)	
C5—C4—C3	107.0 (3)	O3—C9—C7	114.6 (3)	
C5—C4—C7	102.1 (3)			
O1—C2—C3—C4	-177.1 (3)	C8—C7—C9—O3	93.2 (3)	
C8—C7—C9—O2	-83.1 (4)	C4—C7—C9—O3	-141.3 (3)	
C4—C7—C9—O2	42.4 (4)	C1—C7—C9—O3	-35.5 (4)	
C1—C7—C9—O2	148.2 (3)			
D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O1 ⁱ	0.87 (4)	1.86 (4)	2.698 (3)	162 (4)

Symmetry code: (i) $x, y - 1, z$.

All non-carboxyl H atoms, although found in electron-density difference maps, were replaced in calculated positions and allowed to refine as riding models; their displacement parameters were allowed to refine, with the methine H4 atom having $U_{\text{iso}} = 0.060$ and all the methylene H atoms (H3A–H6B) having a group $U_{\text{iso}} = 0.077$. The H atoms of both methyl groups were treated as disordered, with two different sets of three H atoms each; the C8 group H atoms (occupancy ratio 78/22) had a group $U_{\text{iso}} = 0.053$ and the C10 group H atoms (occupancy ratio 73/27) had a group $U_{\text{iso}} = 0.073$. The carboxyl H3 atom was found in an electron-density difference map. Its positional parameters were refined and its isotropic displacement parameter U_{iso} was refined to 0.09 (1).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1292). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bartlett, P. D. & Knox, L. H. (1973). *Org. Synth. Collect.* **5**, 689–691.
- Beilsteins Handbuch der Organischen Chemie (1972). Vol. 10, 3rd suppl., pp. 2914–2915. Berlin/New York: Springer-Verlag.
- Bertolasi, V., Ferretti, V. & Gilli, G. (1982). *Cryst. Struct. Commun.* **11**, 1459–1465.
- Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.
- Carpy, A., Goursolle, M. & Leger, J. M. (1980). *Acta Cryst.* **B36**, 1706–1708.
- Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). *Acta Cryst.* **C52**, 684–687.
- Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1997). Unpublished results.
- Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Fortier, S., DeTitta, G. T., Fronckowiak, M., Smith, G. D. & Hauptman, H. A. (1979). *Acta Cryst.* **B35**, 2062–2066.
- Jones, R. E. & Templeton, D. H. (1958). *Acta Cryst.* **11**, 484–487.
- Lalancette, R. A., Vanderhoff, P. A. & Thompson, H. W. (1991). *Acta Cryst.* **C47**, 132–136.
- Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
- Nahringbauer, I. (1978). *Acta Cryst.* **B34**, 315–318.
- Preut, H., Kreiser, W., Muller, T. & Jones, P. G. (1985). *Acta Cryst.* **C41**, 1480–1482.
- Sheldrick, G. M. (1994). *SHELXTL Users Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* **C48**, 66–70.

Acta Cryst. (1997). **C53**, 372–374

2-(3-Methoxy-2-hydroxyphenyl)benzimidazole

YALÇIN ELERMAN AND MEHMET KABAK

Department of Engineering Physics, Faculty of Sciences,
University of Ankara, 06100 Besevler, Ankara, Turkey.
E-mail: elerman@science.ankara.edu.tr

(Received 15 February 1996; accepted 8 November 1996)

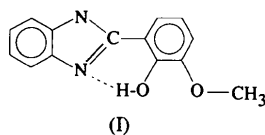
Abstract

Molecules of the title compound, 2-(1,3-benzimidazol-2-yl)-6-methoxyphenol, C₁₄H₁₂N₂O₂, are nearly planar, the greatest deviations from the molecular least-squares plane being -0.145 (3) Å for C12 and -0.149 (3) Å for C14. An intramolecular O—H...N hydrogen bond [O1...N1 2.577 (6) Å] is observed.

Comment

Schiff bases provide a large class of compounds of both stereochemical and magnetochemical interest (Garnovski, Nivorozhkin & Minkin, 1993; Maggio, Pizzino & Romano, 1974; Morassi, Bertini & Sacconi, 1973; Elerman, Fuess & Paulus, 1992). Complexes of Schiff

bases can be classified according to their photochromic and thermochromic characteristics (Cohen, Schmidt & Flavian, 1964; Moustakali, Mavridis, Hadjoudis & Mavridis, 1978; Hadjoudis, Vitterakis, Moustakali & Mavridis, 1987). The intramolecular hydrogen bond between O and N atoms plays an important role in the formation of metal complexes and in the solid state, Schiff base compounds can undergo proton transfer from the hydroxyl O atom to the imine N atom (Moustakali, Mavridis, Hadjoudis & Mavridis, 1978; Hadjoudis, Vitterakis, Moustakali & Mavridis, 1987; Xu, You, Sun, Wang & Liu, 1994). Proton transfer may also be the basis of molecular switches; the charge transport occurs through overlapping π orbitals (Xu *et al.*, 1994). The molecular geometry of the title compound, (I), is illustrated in Fig. 1.



The N1—C7 distance of 1.325 (5) Å corresponds to a typical N=C double bond [*cf.* 1.317 (6) (Elerman, Elmali, Atakol & Svoboda, 1995) and 1.323 (7) Å (Chinnakali, Sivakumar & Natarajan, 1990)]. The O1—C1 bond length of 1.353 (4) Å is in the range observed for similar structures (Inabe, Hoshino, Mitani & Maruyama, 1989; Bregman, Leiserowitz & Schmidt, 1964).

An intramolecular hydrogen bond occurs between the O1 and N1 atoms, the H atom being bonded to the former. The O1...N1, N1...HO1 and O1—HO1 bond distances are 2.577 (6), 1.73 (5) and 0.95 (5) Å, respectively, and the O1—HO1...N1 bond angle is 151 (3)°; the O1...N1 distance is comparable to that observed for thermochromic 2,2'-azinodimethyldiphenol (2.611 Å; Xu *et al.*, 1994) and for *N,N'*-disalicylidene-

1,6-pyrenediamine (2.614 Å; Inabe, Hoshino, Mitani & Maruyama, 1989). As a result of hydrogen bonding between the N1 and O1 atoms, the N1—C8 bond length appears to be longer than N2—C13 [1.391 (5) *versus* 1.376 (5) Å] and the valence angle at the N1 atom is smaller than that at the N2 atom [106.1 (3) *versus* 107.6 (3)°]. The C1—C6—C7—N1 and C5—C6—C7—N2 torsion angles of 6.3 (3) and 7.3 (3)°, respectively, are similar and the molecule is slightly twisted about the C6—C7 bond. Calculations on the non-H atoms show that these lie almost in a plane, with the greatest deviations being -0.145 (3) Å for C12 and -0.149 (3) Å for C14. The dihedral angle between the benzimidazolyl and 3-methoxyphenol groups is 7.50 (7)°.

In thermochromic Schiff base compounds, the planarity of the molecule makes it possible for the proton to transfer through the hydrogen bond in the ground state (Bregman, Leiserowitz & Schmidt, 1964; Bregman, Leiserowitz & Osaki, 1964). This proton transfer, accompanied by a configurational change of the π -electron structure, is central to many proposals for molecular-electronic devices. On the basis of the structural results, the title compound is expected to be a thermochromic Schiff base and may be a candidate for the construction of a type of conductive organic material in which proton transfer is essentially correlated with electron conduction.

Experimental

Benzimidazole and 3-methoxyphenol were dissolved in acetonitrile and the solution refluxed for 2 d. Suitable crystals were obtained upon cooling.

Crystal data

C₁₄H₁₂N₂O₂
M_r = 240.26
 Monoclinic
*P*2₁/*n*
a = 7.737 (1) Å
b = 12.249 (1) Å
c = 12.247 (1) Å
 β = 94.17 (1)°
V = 1157.6 (2) Å³
Z = 4
D_x = 1.38 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 3.3–15.9°
 μ = 0.094 mm⁻¹
T = 293 (2) K
 Needle
 0.20 × 0.12 × 0.08 mm
 Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 1402 measured reflections
 1401 independent reflections
 1099 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.0045
 θ_{\max} = 23.9°
h = -8 → 8
k = 0 → 13
l = 0 → 13
 3 standard reflections
 frequency: 120 min
 intensity decay: 3.8%

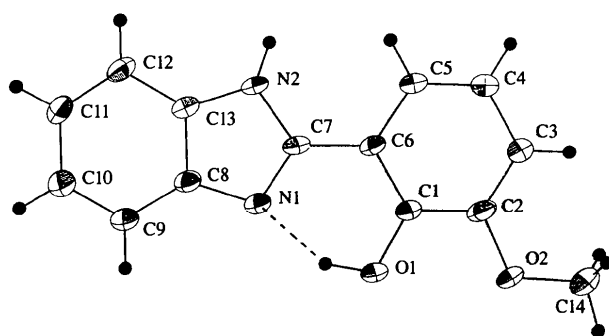


Fig. 1. ORTEP view (Johnson, 1976) of the structure of the title compound showing displacement ellipsoids at the 50% probability level. H atoms have small arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.

Refinement

Refinement on F^2 $R(F) = 0.058$ $wR(F^2) = 0.152$ $S = 1.099$

1401 reflections

166 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.08P)^2 + 1.012P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.353 (4)	N1—C8	1.391 (5)
O2—C2	1.377 (4)	N2—C7	1.371 (4)
O2—C14	1.419 (5)	N2—C13	1.376 (5)
N1—C7	1.325 (5)		
C2—O2—C14	117.1 (3)	C7—N2—C13	107.6 (3)
C7—N1—C8	106.1 (3)		

Non-H atoms were refined anisotropically and H atoms (except for HO1 which was refined positionally with a fixed U_{iso} value) were located geometrically and not refined.

Data collection: CAD-4 Software (Enraf-Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: SDP-Plus (Frenz, 1985). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

The authors wish to acknowledge the purchase of CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Council of Turkey.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- 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.
- Chinnakali, K., Sivakumar, K. & Natarajan, S. (1990). *Acta Cryst.* **C46**, 405–407.
- Cohen, M. D., Schmidt, G. M. J. & Flavian, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
- Elerman, Y., Elmali, A., Atakol, O. & Svoboda, I. (1995). *Acta Cryst.* **C51**, 2344–2346.
- Elerman, Y., Fuess, H. & Paulus, E. F. (1992). *Acta Cryst.* **C48**, 40–42.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Frenz, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
- Garnovski, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–65.
- Hadjoudis, E., Vitterakis, M., Moustakali, I. & Mavridis, A. (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). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Maggio, F., Pizzino, T. & Romano, V. (1974). *Inorg. Nucl. Chem. Lett.* **10**, 1005–1008.
- Morassi, R., Bertini, I. & Sacconi, L. (1973). *Coord. Chem. Rev.* **11**, 343–369.
- Moustakali, I., Mavridis, I., Hadjoudis, E. & Mavridis, A. (1978). *Acta Cryst.* **B34**, 3709–3715.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Xu, X., You, X., Sun, Z., Wang, X. & Liu, H. (1994). *Acta Cryst.* **C50**, 1169–1171.

Acta Cryst. (1997). **C53**, 374–376

3-Hydroxy-*N,N*-dimethyl-2-butenethioamide

KAZUMASA HONDA AND TOHRU TSUCHIYA

National Institute of Materials and Chemical Research,
Tsukuba, Ibaraki 305, Japan. E-mail: honda@nimc.go.jp

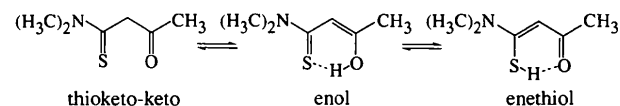
(Received 19 August 1996; accepted 4 November 1996)

Abstract

The title compound, C₆H₁₁NOS, is a 3-oxothioketone. It adopts an enol constitution which is stabilized by an intramolecular O—H···S hydrogen bond [O···S 2.895 (4) Å], even though some molecular orbital calculations suggested that the corresponding enethiol tautomer was the most stable for 3-oxothioketone molecules. A Cambridge Structural Database search for the 3-oxothioketone skeleton found four enol structures but no enethiol ones. The molecule lies on the crystallographic mirror plane.

Comment

The present work is part of a study of the novel reaction of bis(trimethylsilyl)thio ketene and *N,N*-disubstituted amides (Tsuchiya, Oishi, Shibuya, Taguchi & Honda, 1996). The investigated compound is a 3-oxothio ketone which has three possible tautomers, namely, the thioketo-keto, enol and enethiol forms.



For similar 3-oxothio ketone structures such as thioacetylacetone and thiomalondialdehyde, some molecular orbital calculations predicted that the intramolecular hydrogen-bonded enethiol and enol tautomers were