

Acta Cryst. (1999). **C55**, 1691–1692

4-Chloro-2-(4-oxopent-2-en-2-ylamino)-phenol

CENGİZ ARICI,^a M. NAWAZ TAHIR,^a DİNÇER ÜLKÜ^a AND ORHAN ATAKOL^b

^aDepartment of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and ^bDepartment of Chemistry, Ankara University, Tandoğan 06100, Ankara, Turkey. E-mail: dulku@tidya.cc.hun.edu.tr

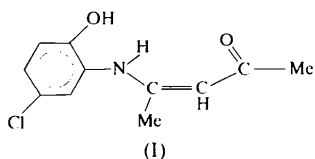
(Received 6 April 1999; accepted 23 June 1999)

Abstract

In the title compound, C₁₁H₁₂ClNO₂, there is an intramolecular hydrogen bond between the amino group and the carbonyl O atom [N···O 2.686 (3) Å]. Additional intermolecular hydrogen bonds between the phenol O atom and the carbonyl groups of neighbouring molecules [O···O 2.634 (2) Å] form a polymeric chain. The molecule is not planar. The dihedral angle between the aromatic ring and the bidentate Schiff base moiety is 44.51 (7)°. The characteristic Schiff base N—C bond length is 1.339 (3) Å.

Comment

Schiff base ligands are used to synthesize new organometallic compounds. They are also widely used in dyes. The title compound, (I), is a newly synthesized Schiff base which could be utilized in obtaining new complexes. A comparison of the title compound with bis[4-(5-chloro-2-hydroxyphenylimino)-2-penten-2-olato(2-)]dicopper(II) (Tahir *et al.*, 1996) confirms the structure.



The title compound contains four molecules in the monoclinic unit cell. The crystal structure is stabilized by one intramolecular N—H···O₂ and one intermolecular O₁—H···O₂ⁱ hydrogen bond [symmetry code: (i) $\frac{1}{2} + x, -\frac{1}{2} - y, z$]. Atoms O₁, Cl and N₁ are almost coplanar with the six-membered aromatic ring (C₁—C₆) (Fig. 1). The distances of O₁, Cl and N₁ atoms from the plane of the aromatic ring are 0.030 (1), 0.0343 (6) and -0.004 (1) Å, respectively. The N₁—C₇—C₈—C₉—O₂ moiety is also planar. The intramolecular hydrogen bond between N₁ and O₂ has an N···O

distance of 2.686 (3) Å. This distance is longer than the intramolecular hydrogen bonds observed in other free Schiff bases such as 5-chloro-2-[(2-hydroxybenzylidene)aminomethyl]phenol (Kevran *et al.*, 1996) and *N*-*n*-propyl-2-oxo-1-naphthylidenemethylamine (Kaitner & Pavlović, 1996); the intramolecular N···O hydrogen-bond distances are 2.599 (3) and 2.578 (2) Å, respectively. The two methyl C atoms, C₁₀ and C₁₁, are -0.070 (2) and -0.108 (2) Å from the best plane of this moiety. The dihedral angle between the aromatic ring (C₁—C₆) and the best plane through the N₁—C₇—C₈—C₉—O₂ plane is 44.51 (7)°, so that the whole molecule is not planar.

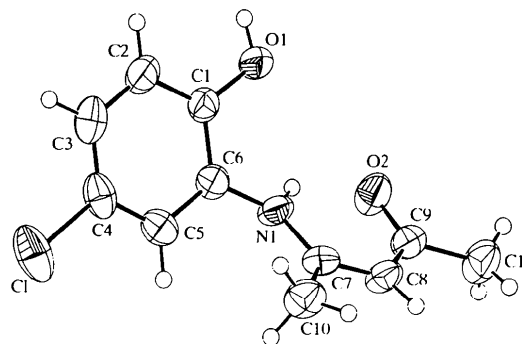


Fig. 1. PLATON (Spek, 1999) drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

The C—C distances in the aromatic ring have expected values [average 1.382 (2) Å]. The bond lengths of the substituents in the six-membered ring [C₁—O₁ 1.353 (3) Å and C₄—Cl 1.743 (2) Å] have similar values to those reported for other Schiff bases (Kevran *et al.*, 1996, and references therein). The methyl C atoms have equal distances to their respective bonded C atoms [C₇—C₁₀ 1.496 (3) Å and C₉—C₁₁ 1.499 (4) Å]. The N₁—C₇ bond, which is characteristic of a Schiff base, is 1.339 (3) Å. The intermolecular hydrogen bond between O₁ and O₂ⁱ, with an O···O distance of 2.634 (2) Å, links the molecules in the unit cell.

Experimental

To a solution of 2-amino-4-chlorophenol (1.435 g, 10 mmol) in ethanol (30 ml), a solution of 2,4-pentanedione (1 g, 10 mmol) in ethanol (20 ml) was added and the mixture heated to boiling. The resulting mixture was set aside for 2 d at 288 K. Light-yellow prismatic crystals were filtered off and dried in air.

Crystal data

C₁₁H₁₂ClNO₂
M_r = 225.677

Mo K α radiation
 λ = 0.71073 Å

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

Monoclinic
*P*2₁/*a*
a = 10.1911 (11) Å
b = 11.3039 (13) Å
c = 11.0983 (11) Å
 β = 115.830 (2)°
V = 1150.8 (2) Å³
Z = 4
*D*_x = 1.302 Mg m⁻³
*D*_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction:
 ψ scan empirical via ψ
scans (Fair, 1990)
*T*_{min} = 0.928, *T*_{max} = 0.939
2265 measured reflections
2019 independent reflections

Cell parameters from 25
reflections
 θ = 11.47–20.92°
 μ = 0.309 mm⁻¹
T = 295 K
Prismatic
0.40 × 0.25 × 0.20 mm
Light yellow

1557 reflections with
I > 3 σ (*I*)
*R*_{int} = 0.010
 θ _{max} = 25.04°
h = 0 → 12
k = 0 → 13
l = -13 → 11
3 standard reflections
frequency: 120 min
intensity decay: -1.16%

Refinement

Refinement on *F*²
R = 0.036
wR = 0.045
S = 0.96
1557 reflections
136 parameters
H atoms constrained
w = 1/[σ ²*F*² + (0.02*F*)²
+ 1.0], except *w* = 0
if *F*² < 3 σ ²

(Δ/σ)_{max} < 0.001
 $\Delta\rho$ _{max} = 0.193 e Å⁻³
 $\Delta\rho$ _{min} = -0.198 e Å⁻³
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Cl—C4	1.743 (2)	N1—C7	1.339 (3)
O1—C1	1.353 (3)	C7—C10	1.496 (3)
O2—C9	1.256 (3)	C9—C11	1.499 (4)
N1—C6	1.418 (3)		
C6—N1—C7	128.9 (2)	N1—C6—C5	122.7 (2)
O1—C1—C2	123.2 (2)	N1—C7—C8	121.0 (2)
O1—C1—C6	117.5 (2)	N1—C7—C10	119.9 (2)
Cl—C4—C3	119.6 (2)	O2—C9—C8	123.0 (2)
Cl—C4—C5	118.9 (2)	O2—C9—C11	118.8 (2)
N1—C6—C1	117.5 (2)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O2 ⁱ	0.83	1.80	2.634 (2)	178
N1—H1 ⁱ ...O2	0.86	1.97	2.686 (3)	139

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* (Giacovazzo, 1980). Program(s) used to refine structure: *MolEN*. Molecular graphics: *PLATON99* (Spek, 1999). Software used to prepare material for publication: *MolEN*.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1291). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Giacovazzo, C. (1980). *Acta Cryst.* **A36**, 362–372.
Kaitner, B. & Pavlović, G. (1996). *Acta Cryst.* **C52**, 2573–2575.
Kevran, S., Elmali, A. & Elerman, Y. (1996). *Acta Cryst.* **C52**, 3256–3258.
Spek, A. L. (1999). *PLATON99. Molecular Geometry Program*. University of Utrecht, The Netherlands.
Tahir, M. N., Ülkü, D., Atakol, O. & Akay, A. (1996). *Acta Cryst.* **C52**, 2676–2678.

Acta Cryst. (1999). **C55**, 1692–1698

'Push–pull' effects in nitroethenamines

ANTHONY LINDEN,^a DALLY MOYA ARGILAGOS,^a HEINZ HEIMGARTNER,^a MARÍA I. GARCÍA TRIMIÑO^b AND ARTURO MACÍAS CABRERA^c

^a*Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland,*
^b*Laboratorios MedSol, Avenida 23e/ 264 y 266, Siboney, Havana, Cuba, and*
^c*Centro Nacional de Investigaciones Científicas (CNIC), Avenida 25, No. 15208, Cubanacán, AP 6990, Havana, Cuba. E-mail: alinden@oci.unizh.ch*

(Received 2 March 1999; accepted 17 May 1999)

Abstract

(*E*)-*N*-methyl-1-(methylthio)-2-nitroethenamine, C₄H₈N₂-O₂S, is a near-planar molecule with significant π -electron delocalization from the ethylene bond into the enamine C—N bond. In the two nitrothioacrylamide derivatives, *N*-benzoyl-3,3-bis(methylamino)-2-nitrothioacrylamide, C₁₂H₁₄N₄O₃S, and *N*-cinnamoyl-3,3-bis(dimethylamino)-2-nitrothioacrylamide, C₁₆H₂₀N₄O₃S, the formal ethylene bond has single-bond properties with a length of about 1.49 Å, while the magnitudes of the torsion angles about this bond approach 90°. The enamine N—C bonds have significant double-bond character and there is significant electron delocalization in the nitrothioacrylamide moiety of each molecule. These compounds can be described as 'push–pull' ethylenes rather than as enamines and are best represented by a zwitterionic formulation in which the charges are accumulated near the opposite ends of the ethylene bond. A strong intramolecular hydrogen bond involving the amide and nitro groups in each compound maintains a rigid confor-