We gratefully acknowledge support for LJF by PPG, Inc. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1369). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Dobson, A. J. & Gerkin, R. E. (1996). *Acta Cryst.* C**52**, 3078–3081.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Veerapandian, B., Salunke, D. M. & Vijayan, M. (1984). *Acta Cryst.* C**40**, 500–502.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

Acta Cryst. (1998). C**54**, 539–540

8-Hydroxyquinolinium–Salicylate–Salicylic Acid (1/1/1) Complex, $C_9H_8NO^+.C_7H_5O_3^-.C_7H_6O_3$

Justin Robert Jebamony and Packianathan Thomas Muthiah

Department of Chemistry, Bharathidasan University, Tiruchirapalli 620 024, Tamil Nadu, India. E-mail: sysop/trichi@dartmail.dartnet.com

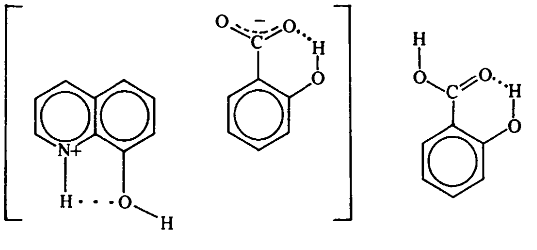
(*Received 1 July 1997; accepted 17 October 1997*)

Abstract

An intramolecular N1—H···O hydrogen bond is present in the 8-hydroxyquinolinium cation. An intramolecular hydrogen bond is present in each of the salicyl moieties (between the phenolic OH and the carboxy group). The crystal structure is stabilized by a network of intermolecular N—H···O, O—H···O and C—H···O hydrogen bonds.

Comment

Oxine (8-hydroxyquinoline) is a widely used analytical reagent. This moiety is also present in many anti-amoebic drugs. The present study has been undertaken as part of our research program on the hydrogen-bonding patterns and interactions in the crystal structures of oxines, their derivatives and their complexes in a variety of crystalline environments (Balasubramanian & Thomas Muthiah, 1996*a*,*b*). In the present study, a 1:2 complex, (I), of 8-hydroxyquinoline and salicylic acid, a widely used analgesic, has been prepared by mixing methanolic solutions of these two compounds in the molar ratio 1:2.



(I)

The asymmetric unit consists of one salicylic acid molecule, one salicylate anion and one 8-hydroxyquinolinium cation. 8-Hydroxyquinolinium is protonated at N1 leading to an enhancement of the internal angle at N1 compared with neutral quinoline moieties. The protonation also increases the difference between the external angles at C8 (Balasubramanian & Thomas Muthiah, 1996*b*). This is thought to have been caused by the intramolecular hydrogen bond, N1—H···O8. This intramolecular contact has also been observed in other 8-hydroxyquinoline structures (Banerjee *et al.*, 1984;

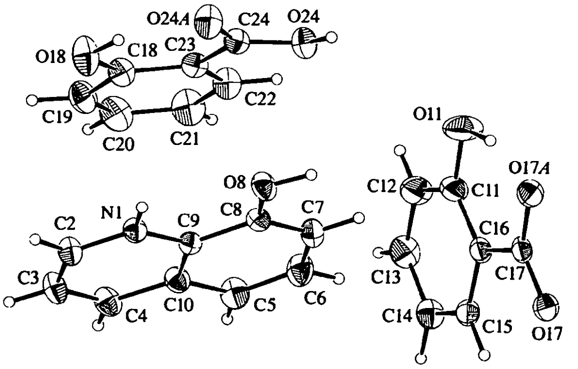


Fig. 1. An *ORTEP* (Johnson, 1965) view of the title compound with displacement ellipsoids at the 50% probability level.

Balasubramanian & Thomas Muthiah, 1996*a*,*b*). N1—H also makes another hydrogen bond with the carbonyl O atom of the carboxylic acid group of salicylic acid.

The intramolecular hydrogen bond (between the phenolic OH and the carboxy group) reported in the crystal structure of salicylic acid (Sundaralingam & Jensen, 1965) is observed in both the salicyl moieties of (I). The carboxy group makes a dihedral angle of 1.97 (7)° with the phenyl ring in the salicylate anion, the corresponding angle being 5.5 (1)° in the salicylic acid moiety. The hydroxy group of the oxine moiety makes a hydrogen bond with one of the O atoms of the carboxylate group of the salicylate anion. The carboxylic acid group of the salicylic acid forms a hydrogen bond with the carboxylate group of the salicylate anion. This type of carboxy–carboxylate interaction has been observed in the crystal structures of many acid salts and proteins (Sawyer & James, 1982). There is also a C—H···O-type interaction (Jeffrey & Saenger, 1991).

Experimental

The synthesis of (I) was carried out by heating 8-hydroxyquinoline and salicylic acid (molar ratio 1:2) in methanol.

Crystal data

$C_9H_8NO^+.C_7H_5O_3^-.C_7H_6O_3$
$M_r = 421.39$
Triclinic
$P\bar{1}$
$a = 9.8899\,(13)$ Å
$b = 10.1168\,(10)$ Å
$c = 10.5673\,(9)$ Å
$\alpha = 86.702\,(9)°$
$\beta = 88.222\,(11)°$
$\gamma = 72.206\,(9)°$
$V = 1005.0\,(2)$ Å^3
$Z = 2$
$D_x = 1.393$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2$–$25°$
$\mu = 0.104$ mm^{-1}
$T = 293\,(2)$ K
Thick plate
0.40 × 0.40 × 0.35 mm
Green–yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3737 measured reflections
3512 independent reflections
3103 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.007$

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 60 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.009$
$S = 1.044$
3512 reflections
357 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.1721P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.162$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.131$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.042 (3)
Scattering factors from *SHELXL*93

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

N1—C2	1.324 (2)	O17*A*—C17	1.2665 (15)
N1—C9	1.367 (2)	O18—C18	1.348 (2)
O8—C8	1.3428 (15)	O24—C24	1.299 (2)
O11—C11	1.352 (2)	O24*A*—C24	1.235 (2)
O17—C17	1.260 (2)		
C2—N1—C9	123.03 (11)	O17—C17—C16	118.27 (11)
O8—C8—C7	125.84 (11)	O17*A*—C17—C16	118.32 (11)
O8—C8—C9	115.83 (11)	O18—C18—C19	117.33 (13)
O11—C11—C12	118.75 (13)	O18—C18—C23	122.85 (12)
O11—C11—C16	121.40 (12)	O24*A*—C24—O24	122.75 (12)
C12—C11—C16	119.84 (13)	O24*A*—C24—C23	121.36 (12)
C15—C16—C11	118.42 (12)	O24—C24—C23	115.89 (11)
O17—C17—O17*A*	123.41 (11)		

All the H atoms were located in the difference Fourier map and refined. *MolEN* (Fair, 1990) was used for the data collection and reduction processes. For structure solution and refinement, *SHELXS*86 (Sheldrick, 1985) and *SHELXL*93 (Sheldrick, 1993) were used, respectively. *PARST* (Nardelli, 1983) was used for geometrical calculations.

The authors thank the Regional Sophisticated Instrumentation Centre, Madras, India (sponsored by the Department of Science and Technology, New Delhi, India), for the data collection. UGC is thanked for financial assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1075). Services for accessing these data are described at the back of the journal.

References

Balasubramanian, T. & Thomas Muthiah, P. (1996*a*). *Acta Cryst.* C**52**, 1017–1019.
Balasubramanian, T. & Thomas Muthiah, P. (1996*b*). *Acta Cryst.* C**52**, 2072–2073.
Banerjee, T., Basak, A. K. & Mazumdar, S. K. (1984). *Acta Cryst.* C**40**, 507–509.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, p. 157. Berlin: Springer.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sawyer, L. & James, M. N. G. (1982). *Nature (London)*, **295**, 79–80.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sundaralingam, M. & Jensen, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.