Norwegian Council of Research (NFR). The structure was presented as a poster at the 16th Nordic Structural Chemistry Meeting in Sigtuna, Sweden, in January 1998, thanks to financial support from the conference organizers, as well as from *Acta Chemica Scandinavica.*

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1052). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.
Campanelli, A. R., Candeloro de Sanctis, S., Giglio, E. & Petriconi, S. (1984). *Acta Cryst.* C**40**, 631–635.
Cerrini, S., Pochetti, G., Gallese, F. & Possagno, E. (1993). *Acta Cryst.* C**49**, 1087–1092.
Coiro, V. M., Giglio, E., Morosetti, S. & Palleschi, A. (1980). *Acta Cryst.* B**36**, 1478–1480.
Giglio, E. & Quagliata, C. (1975). *Acta Cryst.* B**31**, 743–746.
Klyne, W. & Prelog, V. (1960). *Experientia*, **16**, 521–523.
Sheldrick, G. M. (1994). *SHELXTL.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS. Empirical Absorption Correction Program.* University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 1115–1117

3,5-Dichloro-4-(imidazolidin-2-ylidene-ammonio)benzoate dihydrate

E. M. Elssfah,[a] K. Chinnakali,[a]† Hoong-Kun Fun,[a] I. W. Mathison,[b] E. K. Gan,[c] M. Zubaid,[c] T. W. Sam[d] and C. Y. Tan[d]

[a]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia,* [b]*College of Pharmacy, Ferris State University, Big Rapids, MI 49307, USA,* [c]*School of Pharmaceutical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and* [d]*School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

(*Received 18 August 1998; accepted 8 March 1999*)

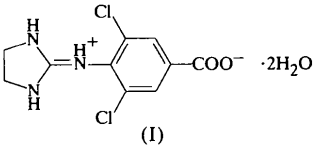
Abstract

The title compound, $C_{10}H_9Cl_2N_3O_2{\cdot}2H_2O$, exists in the zwitterionic form as a result of proton transfer from the carboxylic acid group to the bridging nitrogen. The imidazolidine ring adopts a half-chair conformation. The dihedral angle between the imidazolidine and phenyl rings is 67.29 (6)°, and the carboxyl group is twisted by 5.4 (1)° from the phenyl ring. The crystal structure is stabilized by a network of hydrogen bonds involving the two water molecules.

Comment

Clonidine, an imidazolidine derivative is one of the centrally acting antihypertensive drugs which act primarily *via* α-adrenoceptors in the brain. Quantitative structure–activity studies suggest that the antihypertensive activity of this molecule is governed by distinct steric and electronic characteristics (van Zwieten *et al.*, 1983). In recent years, a large number of imidazolidine derivatives were synthesized in an effort to obtain a more active molecule, but none of them were found to be more potent than clonidine itself.

The title compound, (I), differs from clonidine by the presence of an acid group at the *para*-position of the phenyl ring. Quantitative structure-activity studies showed that hypotensive activity is favoured when small groups are substituted at the *para*-position. Because this compound has a melting point in excess of 573 K and substantial solubility in water, it seemed possible that the compound exists as a zwitterion in the solid state. The X-ray structure determination of this compound was undertaken to evaluate this possibility and to study the molecular conformation.



(I)

The bond lengths and angles in the structure agree very well with those observed in clonidine (Byre *et al.*, 1976; Cody & DeTitta, 1979). The compound is found to be a zwitterion with protonation having occurred at the imino nitrogen. The imidazolidine ring adopts a half-chair conformation with asymmetry parameter ΔC_2(C7) = 0.0108 (8) (Nardelli, 1983); the mean plane through this ring make a dihedral angle of 67.29 (6)° with the phenyl plane. The carboxyl group is twisted by 5.4 (1)° from the phenyl ring [C3—C4—C10—O2 −5.1 (3) and C5—C4—C10—O1 −5.5 (2)°]. In the asymmetric unit, both water molecules are linked to the carboxyl group through O—H···O hydrogen bonds. In the crystal, all the N—H groups are involved in N—H···O intermolecular hydrogen bonds either with water or carboxyl O atoms to form a network structure (Table 2). The water O4 atom acquired full tetra-coordination due to hydrogen bonding.

† On leave from: Department of Physics, Anna University, Chennai 600 025, India.

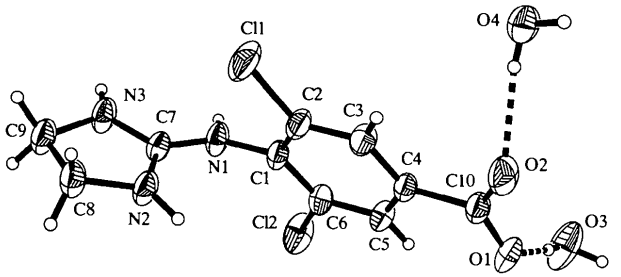


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

2-(4-Carboethoxy-2,6-dichlorophenylimino)imidazolidine was reduced with a tenfold excess of sodium borohydride suspended in boiling *tert*-butyl alcohol following a procedure for the reduction of aromatic ester proposed by Soai *et al.* (1982). Methanol was added dropwise over the period of reduction. Excess reducing agent was destroyed by careful addition of hydrochloric acid. The bulk of the solvent was removed under reduced pressure and the products then partitioned several times between water and ether. 2-(4-Hydroxymethyl-2,6-dichlorophenylimino)imidazolidine was obtained from the ether fraction upon evaporation. The aqueous fraction was concentrated and 2-(4-carboxyl-2,6-dichlorophenylimino)-imidazolidine, *ca* 5% total yield, crystallized from the solution on standing for a few days at 278 K. This amino acid is therefore apparently a by-product of the hydrolsis of ester during the reduction. When the Soai procedure was modified by severely restricting the amount of methanol added dropwise each time, no amino acid by-product was formed.

Crystal data

$C_{10}H_9Cl_2N_3O_2 \cdot 2H_2O$
$M_r = 310.13$
Triclinic
$P\bar{1}$
$a = 8.0857\ (9)$ Å
$b = 8.5118\ (5)$ Å
$c = 10.4161\ (7)$ Å
$\alpha = 88.788\ (7)°$
$\beta = 73.155\ (8)°$
$\gamma = 77.352\ (7)°$
$V = 668.78\ (10)$ Å^3
$Z = 2$
$D_x = 1.540$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 5.439–12.513°$
$\mu = 0.499$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.66 × 0.20 × 0.14 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scans (Siemens, 1994)
$T_{min} = 0.73$, $T_{max} = 0.93$
3721 measured reflections
3073 independent reflections
2298 reflections with $I > 2\sigma(I)$

$R_{int} = 0.018$
$\theta_{max} = 27.50°$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 13$
3 standard reflections every 97 reflections
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.110$
$S = 1.04$
3073 reflections
225 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.0078P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.029 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

O1—C10	1.255 (2)	N2—C7	1.317 (2)
O2—C10	1.250 (2)	N2—C8	1.464 (2)
N1—C7	1.330 (2)	N3—C7	1.334 (2)
N1—C1	1.422 (2)	N3—C9	1.456 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1O3···O1	0.76 (3)	1.99 (3)	2.750 (3)	174 (3)
O4—H2O4···O2	0.80 (3)	1.99 (3)	2.786 (2)	172 (3)
O3—H2O3···O4^{i}	0.83 (4)	1.98 (4)	2.757 (3)	155 (3)
O4—H1O4···O2^{ii}	0.85 (3)	1.96 (3)	2.808 (2)	170 (3)
N1—H1N1···O3^{iii}	0.76 (2)	1.99 (2)	2.732 (2)	167 (2)
N2—H1N2···O1^{iv}	0.91 (2)	1.83 (2)	2.727 (2)	168 (2)
N3—H1N3···O4^{v}	0.85 (2)	2.12 (2)	2.974 (2)	175 (2)
C9—H9A···Cl2^{vi}	0.99 (3)	2.81 (3)	3.538 (2)	131 (2)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 2-y, 2-z$; (iii) $-x, 1-y, 1-z$; (iv) $-x, 2-y, 1-z$; (v) $1-x, 1-y, 1-z$; (vi) $1-x, 1-y, -z$.

All H atoms were located from a difference Fourier map and refined isotropically. The C—H, N—H and O—H distances are in the ranges 0.88 (2)–0.99 (3), 0.76 (2)–0.91 (2) and 0.76 (3)–0.85 (3) Å, respectively. The U_{iso} values of H atoms range from 0.039 (5) to 0.08 (1) Å^2.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

The authors would like to thank the Malaysian Government for research grant R&D No. 190-9609-2801. This work was partially funded by a research grant from Ferris State University, Michigan, USA. KC thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1445). Services for accessing these data are described at the back of the journal.

References

Byre, C., Mosted, A. & Romming, C. (1976). *Acta Chem. Scand. Ser. B*, **30**, 843–846.
Cody, V. & DeTitta, G. (1979). *J. Cryst. Mol. Struct.* **9**, 33–43.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1997). *SHELXTL. Structure Determination Programs*. Version 5.10. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Siemens (1994). *XSCANS User's Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Soai, K., Oyamada, H. & Ookawa, A. (1982). *Synth. Commun.* **12**, 461–467.
Zwieten, P. A. van, Thoolen, M. J. M. C. & Timmermans, P. P. M. W. M. (1983). *Br. J. Clin. Pharm.* **15**, 455S–462S.

Acta Cryst. (1999). C**55**, 1117–1119

(8*RS*,5*SR*,7*SR*)-7-Benzoyl-8-hydroxy-8-phenylspiro[4.5]decan-1-one

H. Surya Prakash Rao,[a] K. Jayalakshmi,[a] Kandasamy Chinnakali[b]† and Hoong-Kun Fun[c]

[a]*Department of Chemistry, Pondicherry University, Pondicherry 605 014, India,* [b]*Department of Physics, Anna University, Chennai 600 025, India, and* [c]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

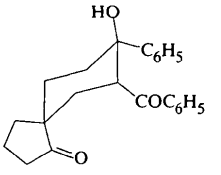
(*Received 25 January 1999; accepted 15 February 1999*)

Abstract

In the title compound, $C_{23}H_{24}O_3$, the five-membered ring adopts a half-chair conformation and the cyclohexane ring is in a chair conformation. The benzoyl group and the phenyl ring are equatorially attached. The hydroxyl group and the benzoyl O atom are involved in an intramolecular O—H···O hydrogen bond. In the crystal, the phenyl rings of the inversion- and screw-related molecules are involved in C—H···π interactions.

Comment

While attempting to develop a facile route to azagonanes, we have isolated not only the expected 1,5-diketone 2-(3-oxo-3-phenylpropyl)-1-cyclopentanone, but also the title compound, (I), in 7% yield from the reaction of phenyl vinyl ketone and cyclopentanone in the presence of barium hydroxide. The importance of this compound comes from the fact that from simple starting materials, such as phenyl vinyl ketone and cyclopentanone, a complex product can be formed which has three stereogenic centres. The stereoselectivity in the reaction is very high, since only one product out of the four enantiomeric pairs has resulted from the reaction. A possible mechanism involves sequential Michael addition, Michael addition and aldol condensation. The X-ray structure determination of (I) was carried out in order to elucidate its molecular conformation.



(I)

Except for C—C bonds involving C17, all bond lengths in (I) show normal values (Allen *et al.*, 1987). The C7—C17 [1.521 (2) Å] and C17—C18 [1.491 (2) Å] bond lengths are longer than normal Csp^2—Csp^3 and Csp^2—Csp^2 bond lengths, which may be due to steric interactions. The bond angles around the spiro-C atom (C5) vary from 99.8 (1) to 113.8 (1)°. Such large deviations from normal sp^3 bond angles have been reported for the spiran junction by Selladurai *et al.* (1995) and Ianelli *et al.* (1992). The spiro planes, C1—C5—C4 and C6—C5—C10, are inclined at 89.6 (1)° to each other. The five-membered ring adopts a half-chair conformation, with C4 and C5 twisted out of the mean plane by 0.229 (2) and −0.234 (2) Å, respectively; asymmetry parameter ΔC_2(C2) = 3.6 (2)° (Duax *et al.*, 1976). The cyclohexane ring adopts a chair conformation, with the C4—C5 bond, the benzoyl group and the phenyl ring attached to it equatorially. The mean plane through the cyclohexane ring forms dihedral angles of 78.1 (1) and 82.68 (9)°, respectively, with the mean planes through the five-membered ring and the phenyl ring. The conformation of the attachment of the benzoyl substituent to the cyclohexane ring is described by the C6—C7—

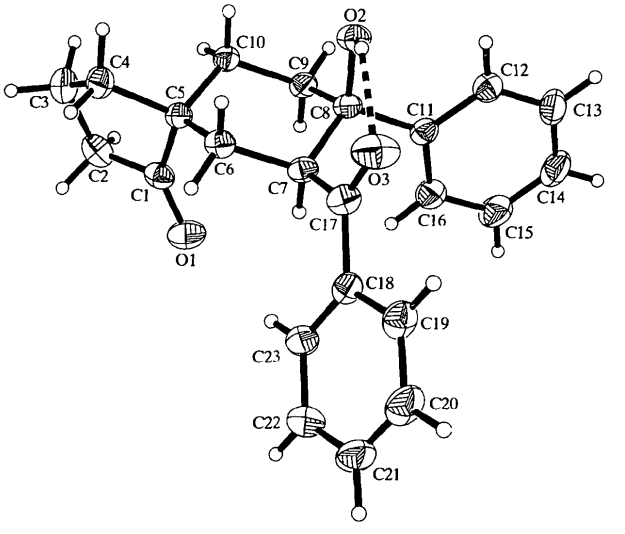


Fig. 1. The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as spheres of arbitrary radii.

† Visiting Postdoctoral Fellow, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.