Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1304). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Anti-Inflammatory Drugs. V. [Tris(2-hydroxymethyl)methyl]ammonium 2-[(2,6-Dichlorophenyl)amino]phenylacetate (TRISH.D)

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Abstract

The structure of the title compound, $C_4H_{12}NO_3^+.C_{14}H_{10}Cl_2NO_2^-$, in the solid state consists of a two-dimensional network of hydrogen-bonded TRISH$^+$ {[tris(2-hydroxymethyl)methyl]ammonium} cations and D$^-$ {2-[(2,6-dichlorophenyl)amino]phenylacetate} anions lined up along the [100] and [010] directions, respectively. Comparisons between the conformations of the TRISH$^+$ cation and the TRIS base ($C_4H_{11}NO_3$) show that the intermolecular hydrogen bonds have a major influence on determining the structures.

Comment

Diclofenac derivatives like the title compound, (I), are powerful anti-inflammatory drugs which are widely used in the form of soluble salts. Thus, as in our previous crystallographic studies on analogous derivatives, attention has been devoted to the relationship between the solid-state conformation of this diclofenac salt and its solubility. Moreover, the interaction between tris(hydroxymethyl)(amino)methane (TRIS) and drugs might be relevant to biochemical studies, since the TRIS buffer is widely used in the physiological pH range 7–9. Other structures of this class of non-steroidal anti-inflammatory drugs determined so far are those of the sodium salt tetrahydrate, NaD.4H_2O (Reck, Faust & Dietz, 1988), the free acid, HD (Moser, Sallmann & Wiesenberg, 1990; Kovala-Demertzi, Mentzafos & Terzis, 1993), the (2-hydroxyethyl)pyrrolidinium salt, EPH.D (Castellari & Sabatino, 1994; Ledwige, Draper, Wilcock & Corrigan, 1996), the (2-hydroxyethyl)pyrrolidinium salt dihydrate, EPHD.2H_2O (Ledwige, Draper, Wilcock & Corrigan, 1996), the bis(2-hydroxyethyl)ammonium salt, NDEAH.D (Castellari & Ottani, 1995), the (2-hydroxyethyl)piperidinium, (2-hydroxyethyl)morpholinium and (2-hydroxyethyl)piperazinium salts, HEPP.D, HEM.D and HEPZ.D, respectively (Castellari & Sabatino, 1996), and the tris(2-hydroxy-

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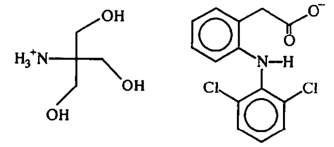
ethyl)ammonium salt, TEAH.D (Castellari & Ottani, 1996). The crystal structure of TRISH.D consists of [tris(2-hydroxymethyl)methyl]ammonium cations and 2-(2,6-dichlorophenylamino)phenylacetate anions joined by hydrogen bonds to form a two-dimensional network along the *ab* plane (Table 2). The structure of this H-aggregate consists of an inner portion containing a double layer of cations arranged in such a way that two enantiomorphs of $TRISH^+$ form a dimer around a symmetry centre of the crystal. The D^- anions [Fig. 1(*b*)] are located on both sides of this double layer and pack along the *c* axis with no short contacts. Intermolecular interactions involve the hydroxymethyl groups and the H atoms of the ammonium group of the cations and the carboxylate group of the anions. The system is stabilized by three types of donor–acceptor interaction, *i.e* $O^-\cdots H_3N^+$, $O^-\cdots H—O$ and $H—O\cdots H_3N^+$. The first two involve neighbouring anions and cations, whereas the third holds together neighbouring cations (Table 2). We note that the three hydroxyl groups interact both as donors and as acceptors. The three H atoms provide four hydrogen-bonding interactions since the H12 atom gives a bifurcated bond. TRISH.D displays low solubility both in water and 1-octanol (Fini, Fazio & Rapaport, 1993). The limited solubility of TRISH.D in water seems to contrast with the presence of three hydrophilic hydroxymethyl groups. However, this behaviour can be rationalized considering that interactions with the solvent do not seem able to substantially alter the H-aggregate (Moser, Sallmann & Wiesenberg, 1990). Solvent molecules compete with the existing solid-state hydrogen-bonding pattern leaving a large number of anions and cations hydrogen-linked together.



(I)

It is of some interest to compare the crystal structure of the $TRISH^+$ cation with the corresponding TRIS base. We have thus redetermined† the structure of TRIS at ambient temperature by refining against F^2.

In the crystal, the TRIS base adopts an asymmetric conformation (Fig. 2). Selected bond lengths and angles are reported in Table 3. Agreement with values obtained at 295 K by Eilerman & Rudman (1980) is within 2σ. Also, the parameters of the intermolecular hydrogen bonds [Fig. 2 (solid lines) and Table 4] are in accord with those reported by the cited authors. Moreover, our X-ray analysis confirms both the large thermal motion of O2 and the short C2—O2 distance, which can be attributed to the lower force field surrounding the O2 atom. In addition, we note the presence of two intramolecular hydrogen bonds involving the amine group [Fig. 2 (dashed lines)]; N1—H1···O1 2.799 (1), 2.52 (2) Å and 101 (2)°, and N2—H2···O2 2.800 (2), 2.51 (2) Å and 103 (2)°. These two intramolecular hydrogen bonds stabilize the molecular conformation whose symmetry can be idealized as C_s if terminal H atoms are ignored. The $TRISH^+$ cation is

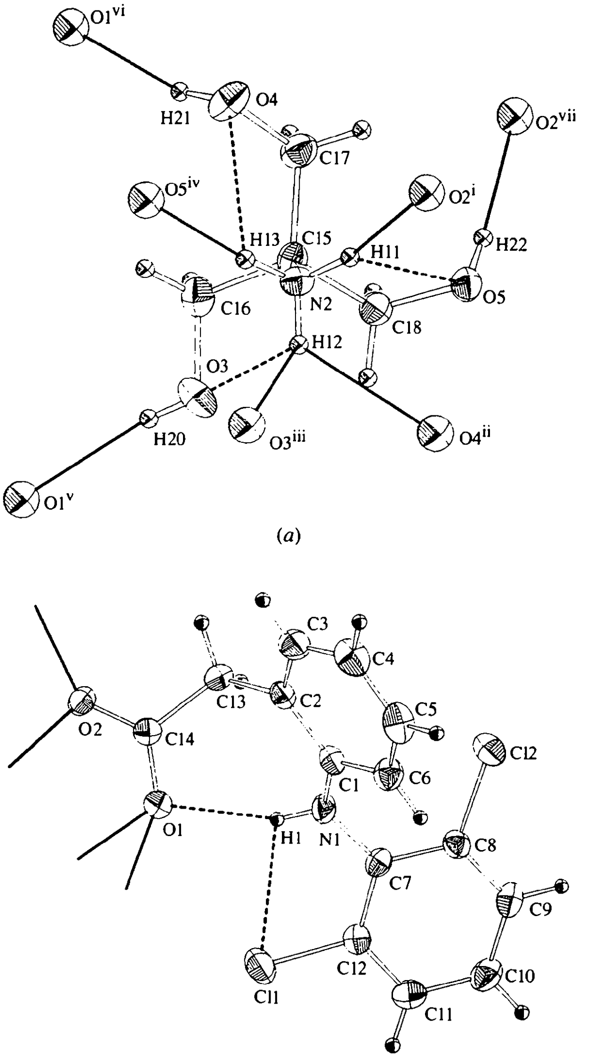


Fig. 1. (*a*) *ORTEP*II (Johnson, 1976) view (50% probability ellipsoids) of the $TRISH^+$ base showing intermolecular (solid lines) and intramolecular (dashed lines) hydrogen bonds. Details of the intermolecular hydrogen bonds are reported in Table 2. (*b*) *ORTEP*II view (50% probability ellipsoids) of the D^- anion showing intermolecular (solid lines) and intramolecular (dashed lines) hydrogen bonds.

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† The crystal structure of TRIS was first reported by Rudman, Eilerman & La Place (1978) in a preliminary work at room temperature. Eilerman & Rudman (1980) then performed a diffraction study not listed in the Cambridge Structural Database (Allen *et al.*, 1991). Other determinations of this crystal structure reported by Kendi (1982) and Xianti, Genbo, Zhengdong & Goufan (1987) present higher values of *R*.

asymmetric in the crystal since the H atoms of the hydroxyl groups adopt unsymmetrical conformations in order to optimize the intermolecular hydrogen bonds. Aside from these H atoms, a propeller-like conformation [Fig. 1(*a*)] with idealized C_3 symmetry can be envisaged. Again, this conformation is stabilized by the presence of three intramolecular hydrogen bonds [Fig. 1(*a*) (dashed lines)]; N2—H11···O5 2.893 (3), 2.64 (2) Å and 97 (2)°, N2—H12···O3 2.819 (3), 2.55 (3) Å and 98 (2)°, and N2—H13···O4 2.796 (3), 2.55 (3) Å and 96 (2)°.

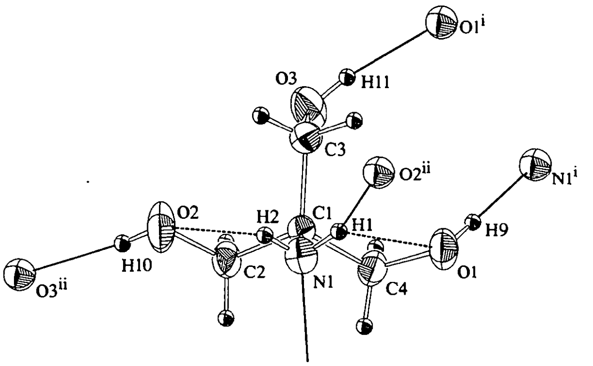

Fig. 2. *ORTEP*II (Johnson, 1976) view (50% probability ellipsoids) of the TRIS base showing intermolecular (solid lines) and intramolecular (dashed lines) hydrogen bonds.

The molecular geometry of the TRISH$^+$ cation is analogous to those reported previously for TRISH$^+$.X^- (X = F, Cl, Br, I; Rudman, Lippman, Sake-Gowda & Eilerman, 1983). It displays a C—N distance of 1.499 (3) Å. This distance is longer than in the neutral TRIS molecule [1.471 (2) Å] and indicates the quadrivalence of the N atom (Rudman, Lippman, Sake-Gowda & Eilerman, 1983). The C—O distance [1.416 (3) Å] is close to the value reported for the TRIS molecule [1.420 (1) Å]. The molecular conformation of the D$^-$ anion is nearly identical to those of analogous diclofenac derivatives. However, the dihedral angle between the two phenyl rings of TRISH.D [59.3 (1)°] is significantly lower than the mean value of 68.00 (4)° found in the other organic salts of diclofenac (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996). It has been demonstrated (Moser, Sallmann & Wiesenberg, 1990) that the dihedral angle between the planes of the two aromatic rings is directly correlated with the anti-inflammatory power of diclofenac analogues. The two rings should be twisted as much as possible in order to optimize the competitive binding of the carboxylate group of the drug to the arachidonic acid substrate which inhibits the cyclooxygenase–arachidonic acid interaction. Thus, the value of this twist angle reported for the present structure, in addition to the scarce lipophilicity of TRISH.D, should confine this compound to the diclofenac-based drugs of weak pharmacological activity.

Experimental

Diclofenac (IBSA, Lugano, Switzerland) was dissolved in methanol. An equivalent amount of tris(2-hydroxymethyl)-(amino)methane (Fluka, Buchs, Switzerland) was added to this solution. Crystals of TRISH.D were grown by slow diffusion of *n*-hexane into a methanol solution of TRISH.D at room temperature.

TRISH.D

Crystal data

$C_4H_{12}NO_3^+.C_{14}H_{10}Cl_2NO_2^-$
$M_r = 417.28$
Monoclinic
$P2_1/a$
$a = 10.152\ (3)$ Å
$b = 9.407\ (3)$ Å
$c = 19.448\ (8)$ Å
$\beta = 90.12\ (3)°$
$V = 1857.3\ (11)$ Å^3
$Z = 4$
$D_x = 1.49$ Mg m^{-3}
$D_m = 1.48$ Mg m^{-3}
D_m measured by flotation in a mixture of 1-bromo-2-chloroethane and *p*-xylene
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 5–11°$
$\mu = 0.383$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.20 × 0.15 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
Absorption correction: none
6488 measured reflections
3258 independent reflections
1804 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0677$
$\theta_{\rm max} = 25.01°$
$h = -12 \rightarrow 12$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 23$
3 standard reflections frequency: 160 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0403$
$wR(F^2) = 0.0866$
$S = 0.996$
3251 reflections
272 parameters
H atoms riding except H1, H11, H12, H13, H20, H21 and H22 for which all parameters were refined
$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.0058P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.069$
$\Delta\rho_{\rm max} = 0.210$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.211$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C7	1.385 (3)	N2—C15	1.499 (3)
N1—C1	1.404 (4)	C15—C17	1.513 (4)
C14—O2	1.240 (3)	C15—C16	1.515 (4)
C14—O1	1.259 (3)	C15—C18	1.526 (4)
C7—N1—C1	125.2 (3)	O2—C14—C13	119.0 (3)
C2—C13—C14	115.2 (2)	O1—C14—C13	118.0 (2)

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

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	2.57 (3)	2.979 (3)	112 (2)
N1—H1···O1	2.10 (3)	2.853 (4)	148 (2)
N2—H11···O2^{i}	1.91 (2)	2.770 (3)	159 (2)

N2—H12···O4^{ii}	2.31 (3)	2.927 (3)	125 (2)
N2—H12···O3^{iii}	2.44 (3)	3.062 (3)	126 (2)
N2—H13···O5^{iv}	2.03 (2)	2.928 (3)	170 (3)
O3—H20···O1^{v}	2.16 (3)	2.934 (3)	171 (3)
O4—H21···O1^{vi}	1.93 (3)	2.731 (3)	161 (4)
O5—H22···O2^{vii}	1.91 (2)	2.717 (3)	172 (3)

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

TRIS

Crystal data

$C_4H_{11}NO_3$
$M_r = 121.14$
Orthorhombic
$Pna2_1$
$a = 8.8435\ (10)$ Å
$b = 8.7911\ (10)$ Å
$c = 7.7906\ (10)$ Å
$V = 605.67\ (12)$ Å^3
$Z = 4$
$D_x = 1.328$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–$25°$
$\mu = 0.112$ mm^{-1}
$T = 293\ (2)$ K
Spherical
0.35 × 0.33 × 0.30 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
Absorption correction: none
2527 measured reflections
1307 independent reflections
1259 reflections with $I > 2\sigma(I)$

$R_{int} = 0.0414$
$\theta_{max} = 26.94°$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -9 \rightarrow 9$
3 standard reflections
frequency: 160 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0320$
$wR(F^2) = 0.0883$
$S = 1.042$
1302 reflections
119 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.0353P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.082$
$\Delta\rho_{max} = 0.198$ e Å^{-3}
$\Delta\rho_{min} = -0.174$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −1.0 (10)

Table 3. *Selected geometric parameters (Å, °) for TRIS*

C1—N1	1.471 (2)	C2—O2	1.411 (2)
C1—C2	1.522 (1)	C3—O3	1.422 (2)
C1—C4	1.524 (2)	C4—O1	1.427 (2)
C1—C3	1.529 (2)		
N1—C1—C2	108.6 (1)	N1—C1—C3	109.4 (1)
N1—C1—C4	108.2 (1)		

Table 4. *Hydrogen-bonding geometry (Å, °) for TRIS*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O1—H9···N1^{i}	1.91 (2)	2.720 (2)	174 (2)
O2—H10···O3^{ii}	1.94 (2)	2.718 (1)	173 (2)
O3—H11···O1^{i}	1.85 (2)	2.674 (2)	171 (2)
N1—H1···O2^{iii}	2.35 (2)	3.043 (2)	142 (2)

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

The H atoms involved in hydrogen bonds were experimentally located and their coordinates and displacement coefficients were isotropically refined. An initial torsion angle of the O—H groups was chosen which maximizes the electron density. In subsequent refinement cycles, these groups were re-idealized with retention of the current torsion angle and with restraints to make all the O—H distances approximately equal (e.s.d. of 0.03 Å). The remaining H atoms were placed in calculated positions and refined riding on parent atoms (aromatic C—H = 0.93 and sp^3 C—H = 0.97 Å). The same procedure was followed for the determination of the structure of the TRIS base. In TRIS, all the H atoms were experimentally located and isotropically refined.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SCHAKAL*92 (Keller, 1992) and *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1262). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 486–488

Two Schiff Base Ligands Derived from 1,2-Diaminoethane

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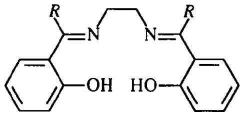
Abstract

The structures of two Schiff base ligands, 2,2′-[(1,2-ethanediyl)bis(nitrilopropylidyne)]bisphenol, $C_{20}H_{24}N_2O_2$, (I), and 2,2′-{(1,2-ethanediyl)bis[nitrilo(phenyl)methylidyne]}bisphenol, $C_{28}H_{24}N_2O_2$, (II), are reported. The molecular structure of (I) is centrosymmetric and therefore has a *trans* conformation. The asymmetric unit for structure (II) contains two molecules, but both have *gauche* arrangements. Structures (I) and (II) both contain the enolimine tautomers and exhibit intramolecular hydrogen bonding.

Comment

Relatively few structural reports have appeared for uncoordinated tetradentate Schiff base ligands (Corden, Errington, Moore & Wallbridge, 1996, and references therein), but a recent report from these laboratories considered the structures of two such ligands derived from 1,2-diaminocyclohexane (Cannadine, Corden, Errington, Moore & Wallbridge, 1996). Two further examples of this type of ligand, (I) and (II), are reported here.



(I) $R = C_2H_5$
(II) $R = \text{Ph}$

The molecular structure of compound (I) is shown in Fig. 1. This structure is centrosymmetric and thus the N atoms have a *trans* conformation. The two aromatic rings are necessarily parallel, but they are only approximately coplanar. Clearly, the enolimine tautomer is favoured rather than the ketamine form. This is evident from the observed O1—C1 bond distance of 1.351 (3) Å, which is consistent with a single bond, and the N1—C7 bond distance of 1.295 (3) Å, which is indicative of a double bond. Furthermore, the O1—N1 distance of 2.501 (3) Å strongly suggests intramolecular hydrogen bonding.

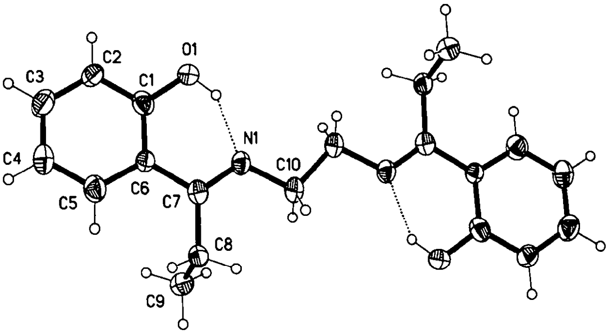


Fig. 1. View of (I) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

The asymmetric unit for structure (II) contains two molecules, one of which is illustrated in Fig. 2. The N—C—C—N torsion angles of −63.4 (6) and 62.5 (6)° (*i.e.* the same absolute values within experimental error) in the two molecules of the asymmetric unit indicate *gauche* conformations but of opposite chirality. The dimensional similarities are further illustrated in Fig. 3 in which the two molecules have been superimposed after inversion of one of the structures; the phenol rings are inclined at an angle of 68.42 (18)° in one molecule, but at an angle of 71.24 (17)° in the other. The absolute structures cannot be reliably determined from the data set. Once again, the bond lengths clearly indicate the presence of both the enolimine tautomer and intramolecular hydrogen bonding.

Clearly the most dramatic difference between structures (I) and (II) is the conformational change; a *trans*

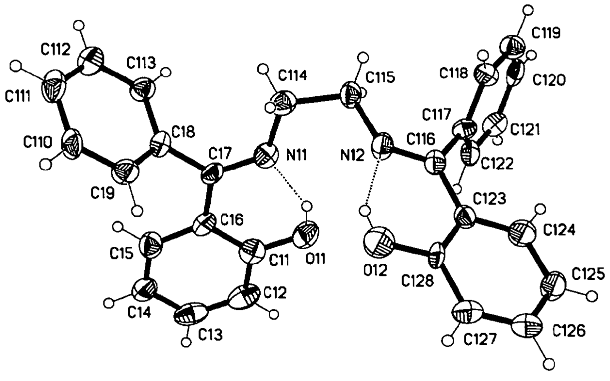


Fig. 2. View of one molecule of (II) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

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