Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Xianti, L., Genbo, S., Zhengdong, L. & Goufan, H. (1987). *Jiegon Huaxue*, **6**, 214.

Acta Cryst. (1997). C**53**, 486–488

Two Schiff Base Ligands Derived from 1,2-Diaminoethane

JONATHAN P. CORDEN, WILLIAM ERRINGTON, PETER MOORE AND MALCOLM G. H. WALLBRIDGE

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England. E-mail: msrpq@csv.warwick.ac.uk

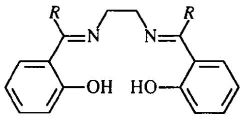
(*Received 5 July 1996; accepted 21 November 1996*)

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 = 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.

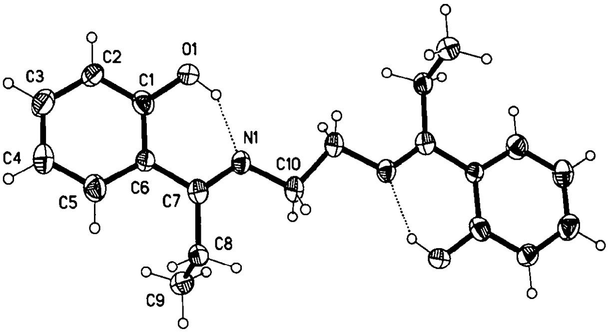


Fig. 1. View of (I) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

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*

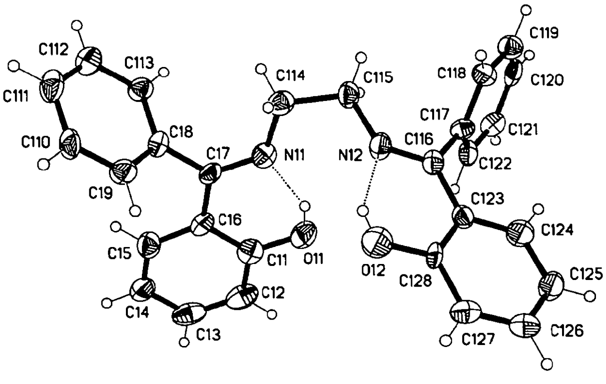


Fig. 2. View of one molecule of (II) showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

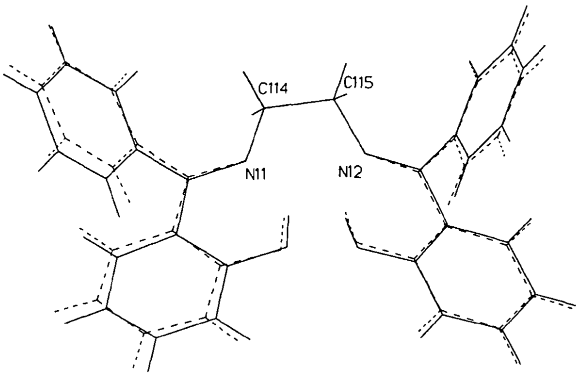


Fig. 3. Superposition of the two molecules in the asymmetric unit of (II).

conformation is observed in (I), but in (II), the two molecules have *gauche* arrangements. This result, however, must not be taken to imply that the conformations observed in the solid state are necessarily the lowest energy conformations; obviously the solid-state conformations must represent a compromise between conformational stability and the overall packing energy.

Experimental

Compound (I) was prepared by the condensation of 2-hydroxypropiophenone (66.5 mmol) with 1,2-diaminoethane (33.25 mmol) in methanol (100 ml). Compound (II) was prepared by the condensation of 2-hydroxybenzophenone (37.9 mmol) with 1,2-diaminoethane (18.9 mmol) in methanol (100 ml). Crystals of both compounds suitable for the X-ray diffraction work were obtained by the slow evaporation of saturated methanolic solutions of the products.

Compound (I)

Crystal data

$C_{20}H_{24}N_2O_2$
$M_r = 324.41$
Monoclinic
$P2_1/c$
$a = 5.131$ (5) Å
$b = 13.261$ (8) Å
$c = 12.718$ (5) Å
$\beta = 94.95$ (8)°
$V = 862.1$ (10) Å^3
$Z = 2$
$D_x = 1.250$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 2.22$–$25.09°$
$\mu = 0.081$ mm^{-1}
$T = 150$ (2) K
Block
0.20 × 0.20 × 0.18 mm
Yellow

Data collection

Delft Instruments FAST TV area detector diffractometer
Flat-plate scans
Absorption correction: none
3778 measured reflections
1324 independent reflections

628 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0748$
$\theta_{\rm max} = 25.09°$
$h = -3 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R(F) = 0.0423$
$wR(F^2) = 0.0927$
$S = 0.723$
1322 reflections
111 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.190$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.151$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.351 (3)	C4—C5	1.384 (3)
N1—C7	1.295 (3)	C5—C6	1.395 (3)
N1—C10	1.471 (3)	C6—C7	1.471 (4)
C1—C2	1.394 (3)	C7—C8	1.505 (4)
C1—C6	1.414 (4)	C8—C9	1.516 (3)
C2—C3	1.381 (4)	C10—C10$^{\rm i}$	1.524 (5)
C3—C4	1.365 (4)		
C7—N1—C10	121.4 (2)	N1—C7—C6	117.3 (2)
O1—C1—C2	118.4 (3)	N1—C7—C8	123.5 (3)
O1—C1—C6	121.6 (3)	C6—C7—C8	119.2 (2)
C5—C6—C7	121.7 (3)	N1—C10—C10$^{\rm i}$	108.4 (3)
O1—C1—C2—C3	−179.6 (2)	N1—C7—C8—C9	−98.0 (3)
C10—N1—C7—C6	−179.2 (2)	C7—N1—C10—C10$^{\rm i}$	−177.6 (3)

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

Compound (II)

Crystal data

$C_{28}H_{24}N_2O_2$
$M_r = 420.49$
Orthorhombic
$Pna2_1$
$a = 18.530$ (8) Å
$b = 13.443$ (10) Å
$c = 17.737$ (8) Å
$V = 4418.3$ (43) Å^3
$Z = 8$
$D_x = 1.264$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 1.87$–$25.15°$
$\mu = 0.080$ mm^{-1}
$T = 150$ (2) K
Needle
0.52 × 0.28 × 0.24 mm
Yellow

Data collection

Delft Instruments FAST TV area detector diffractometer
Flat-plate scans
Absorption correction: none
19 267 measured reflections
6357 independent reflections

2491 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0918$
$\theta_{\rm max} = 25.15°$
$h = -20 \rightarrow 20$
$k = -14 \rightarrow 14$
$l = -13 \rightarrow 19$

Refinement

Refinement on F^2
$R(F) = 0.0394$
$wR(F^2) = 0.0854$
$S = 0.546$
6349 reflections
581 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0172P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.010$

$\Delta\rho_{\rm max} = 0.148$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.165$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −7 (2)

Table 2. *Selected geometric parameters (Å, °) for (II)*

O11—C11	1.350 (6)	O21—C21	1.349 (6)
O12—C128	1.342 (6)	O22—C228	1.359 (6)
N11—C17	1.302 (6)	N21—C27	1.290 (6)
N11—C114	1.480 (6)	N21—C214	1.456 (6)
N12—C116	1.311 (6)	N22—C216	1.292 (6)
N12—C115	1.479 (6)	N22—C215	1.470 (6)
C17—N11—C114	122.8 (5)	O21—C21—C26	121.9 (5)
C116—N12—C115	120.5 (5)	N21—C27—C26	117.6 (5)
O11—C11—C12	117.2 (6)	N21—C27—C28	124.1 (5)
N11—C17—C18	123.6 (5)	N21—C214—C215	110.2 (5)
N11—C17—C16	116.9 (5)	N22—C215—C214	109.1 (5)
N11—C114—C115	110.0 (5)	N22—C216—C223	117.9 (5)
N12—C115—C114	109.0 (5)	N22—C216—C217	122.7 (5)
N12—C116—C123	118.0 (5)	O22—C228—C223	121.2 (6)
N12—C116—C117	122.5 (5)	O22—C228—C227	118.1 (6)
O21—C21—C22	117.9 (6)		
O11—C11—C16—C17	−0.5 (8)		
N11—C114—C115—N12	−63.4 (6)		
C116—C123—C128—O12	−1.4 (9)		
O21—C21—C26—C25	−179.5 (5)		
N21—C214—C215—N22	62.5 (6)		

Data were collected about the ω axis using exposure times of 10 s and frame increments of 0.20°; the crystal-to-detector distance was 4.9 cm. Crystal decay was estimated by comparing the intensities of common reflections at the start and end of data collection and, in both cases, the rate of decay was negligible. The H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms and H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the parent atom.

For both compounds, data collection: *MADNES* (Pflugrath & Messerschmidt, 1992); cell refinement: *MADNES*; data reduction: *SHELXTL-Plus* (Sheldrick, 1991); program(s) used to solve structures: *SHELXTL-Plus*; program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL93*.

The authors wish to thank Professor M. B. Hursthouse and the EPSRC X-ray crystallographic service (University of Wales, Cardiff) for collecting the diffraction data. We also wish to acknowledge the use of the EPSRC's Chemical Database Service (Allen *et al.*, 1991) at Daresbury and BP for financial support (JPC).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: PA1247). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.

Cannadine, J. C., Corden, J. P., Errington, W., Moore, P. & Wallbridge, M. G. H. (1996). *Acta Cryst.* C**52**, 1014–1017.

Corden, J. P., Errington, W., Moore, P. & Wallbridge, M. G. H. (1996). *Acta Cryst.* C**52**, 125–127.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Pflugrath, J. W. & Messerschmidt, A. (1992). *MADNES. Munich Area Detector Systems.* Enraf–Nonius, Delft, The Netherlands.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 488–490

Low-Temperature Phase of Tetraethylammonium Bromide

MARTINA RALLE,[a,c] JEFFREY C. BRYAN,[b] ANTON HABENSCHUSS[c] AND BERNHARD WUNDERLICH[a,c]

[a]*Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA,* [b]*Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, USA, and* [c]*Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6197, USA. E-mail: athas@utk.edu*

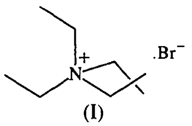
(*Received 30 July 1996; accepted 12 December 1996*)

Abstract

The title compound, $C_8H_{20}N^+.Br^-$, exhibits a trigonal structure. Pairs of alkyl chains form all-*trans* sequences through the N atom.

Comment

Tetra-*n*-alkylammonium bromides and iodides form an interesting series of compounds exhibiting different kinds of disordering transitions depending on alkyl-chain length and temperature. We have been studying the disordering transitions of these materials (up to a chain length of 18 C atoms) using X-ray powder diffraction (Xenopoulos, Ralle, Habenschuss & Wunderlich, 1996; Ralle, Xenopoulos, Habenschuss & Wunderlich, 1996), thermal analysis (Xenopoulos, Cheng, Yasuniva & Wunderlich, 1992; Xenopoulos, Cheng & Wunderlich, 1993) and solid-state NMR (Cheng, Xenopoulos & Wunderlich, 1992*a*,*b*, 1993). The low-temperature crystal structures of tetra-*n*-alkylammonium bromides and iodides containing up to four C atoms per alkyl chain were known for all but the title compound, (I). Solving the crystal structure of the title compound closes an important gap and helps us to complete our study of disorder in these materials.



(I)