within the two condensed tetrahedra is considerably different from that in single (uncondensed) rings. This is the first reported structure in which the O atom axial in relation to the ring is bonded to the P atom by almost a single bond.

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N,N'-Ethylenebis(salicylideneimine)

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Abstract. $C_{16}H_{16}N_2O_2$, $M_r = 268.3$, monoclinic, $P2_1/c$, $a = 6.094$ (6), $b = 7.567$ (6), $c = 30.68$ (2) Å, $\beta = 97.87$ (5)°, $U = 1401.4$ Å^3; $D_c = 1.271$ g cm^{-3}, $Z = 4$; $\mu = 6.69$ cm^{-1} (Cu $K\alpha$). Direct methods were used to determine the structure from three-dimensional X-ray data. Block-diagonal-matrix least-squares refinement, based on 1262 independent reflexions, converged with R at 0.035. The molecules, approximately centrosymmetric, are in the enoliminic form with intramolecular hydrogen bonds.

Introduction. Intensity data were collected on a Siemens diffractometer by the θ–2θ scan technique with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). 2503 independent reflexions were measured in the region $2\theta \leq 60°$ and 1262 with $I > 3\sigma(I)$ were corrected for the Lorentz and polarization effects. No corrections for absorption ($\mu R = 0.7$) or extinction were applied. The scattering factors were those of Moore (1963). A set of 211 E values greater than 2.08 were then used in the direct-methods program of Germain, Main & Woolfson (1971). An E map calculated from one of the best solutions clearly revealed all the non-hydrogen atoms, which were then refined by block-diagonal-matrix least squares, allowing finally for anisotropic thermal motion. The calculated positions of the H atoms well fitted the electron density peaks on the subsequent difference Fourier map. The two H atoms involved in the hydrogen bonds were located directly from the difference map. The final anisotropic refinement, in

which the hydrogen coordinates and their temperature factors (set at $B = 5 \cdot 0$ Å^2) were kept constant, reduced $R = \Sigma (|F_o| - |F_c|)/\Sigma |F_o|$ to $0 \cdot 035$ for the observed reflexions. The atomic parameters and their e.s.d.'s are given in Table 1.* The numbering of the atoms is shown in Fig. 1. Bond lengths, bond angles and some internal rotation angles of interest are shown in Fig. 2. Computations were carried out with programs written by Albano, Domenicano & Vaciago (1966).

Discussion. As part of a research programme on the structural aspects and the bonding mode of metal complexes with quadridentate Schiff bases, like N,N'-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33167 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic positional parameters* ($\times 10^4$; for H $\times 10^3$)

The isotropic temperature factor for hydrogen is fixed at 5 Å^2. Numbers in parentheses are the e.s.d.'s in the least significant digits.

	x	y	z
O(1)	7683 (2)	780 (2)	1755 (0)
O(2)	−2676 (2)	2230 (2)	3223 (0)
N(1)	4111 (3)	1994 (2)	2022 (0)
N(2)	884 (2)	1078 (2)	2938 (0)
C(1)	6708 (3)	1122 (3)	1343 (1)
C(2)	7838 (3)	697 (3)	992 (1)
C(3)	6893 (4)	1028 (3)	571 (1)
C(4)	4798 (4)	1802 (3)	483 (1)
C(5)	3668 (3)	2212 (3)	828 (1)
C(6)	4578 (3)	1881 (2)	1263 (1)
C(7)	3323 (3)	2273 (3)	1623 (1)
C(8)	2735 (3)	2375 (3)	2365 (1)
C(9)	2228 (3)	695 (3)	2590 (1)
C(10)	1709 (3)	785 (3)	3334 (1)
C(11)	499 (3)	1160 (2)	3701 (1)
C(12)	1474 (3)	812 (3)	4129 (1)
C(13)	389 (4)	1190 (3)	4483 (1)
C(14)	−1700 (4)	1950 (3)	4410 (1)
C(15)	−2729 (4)	2305 (3)	3990 (1)
C(16)	−1649 (3)	1902 (3)	3631 (1)
H(1)	680	120	195
H(2)	930	12	105
H(3)	774	73	32
H(4)	413	205	18
H(5)	218	277	77
H(7)	180	276	156
H(10)	322	29	339
H(12)	296	28	418
H(13)	109	92	479
H(14)	−248	225	466
H(15)	−422	286	394
H(16)	−165	180	300
1H(8)	355	321	259
2H(8)	132	296	223
1H(9)	365	11	272
2H(9)	140	−13	237

ethylenebis(salicylideneimine) (salen H$_2$) and its ring-substituted derivatives (Bresciani Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio, 1976), we have determined the crystal structure of the free Schiff base salen H$_2$ in order to detect its structural variations upon
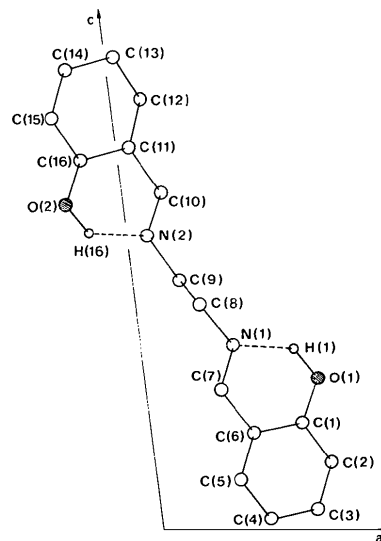

Fig. 1. (010) projection of the molecule with the numbering of the atoms. Only those H atoms involved in hydrogen bonds are shown.
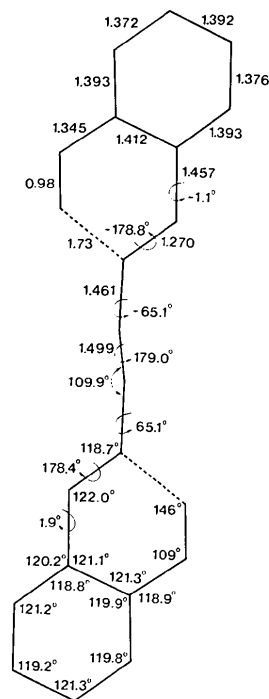

Fig. 2. Average bond lengths (Å) and angles relative to the two chemically equivalent parts of the molecule. Some torsion angles of interest are also given.

coordination and to provide some insight into the conformational behaviour of this kind of ligand.

Bond lengths and angles are in full agreement with the enoliminic structure already suggested to be present in solution (Gullotti, Pasini, Fantucci, Ugo & Gillard, 1972). In fact, the N—CH and O—C distances of 1·270 (3) and 1·345 (3) Å, respectively, are consistent with double N=C and single O—C bonds. Furthermore, the C(6)—C(7) and C(10)—C(11) bond lengths [1·456 (4) and 1·457 (4) Å] are those expected for single bonds between C(sp^2) atoms, and the N—CH$_2$ bond lengths, 1·461 (3) Å, are proper for N(sp^2)—C(sp^3) σ bonds. On the other hand, H(1) and H(16) clearly appeared on the difference map as bound to the O atoms, forming intramolecular hydrogen bonds [O(1)···N(1) 2·596 (2), O(2)···N(2) 2·598 (2) Å]. It is interesting to observe that the enoliminic form has also been found in the solid state for *N,N'*-(*o*-phenylene)bis(salicylideneimine) Schiff base (salph H$_2$) (Bresciani Pahor *et al.*, 1976). The C(1), C(6) and C(11), C(16) benzene rings are planar within ±0·005 and ±0·007 Å, respectively, and the two halves of the molecule, excluding the ethylene bridge atoms, are also planar (within ±0·02 Å) because of the intramolecular hydrogen bonds. The molecules are approximately centrosymmetric, the inversion centre being located at the midpoint of the CH$_2$—CH$_2$ bond. In fact, the ethylenediamine bridge has a *trans* conformation (*T*) (torsion angle of 179·0°) while the internal rotation angles around the N—CH$_2$ bonds are ±65·1° yielding *gauche* conformations (*G,G'*). Thus the C(6)···C(11) chain does not assume, in the solid state, a planar zigzag structure, but rather a *T—G—T—G'—T* conformation corresponding to a minimum in potential energy.

In the crystal the molecules are held together only by van der Waals forces, all contacts being greater than 3·50 Å, so .that any possibility of intermolecular hydrogen bonds is ruled out.

As previously shown, the solid-state molecular structure corresponds to a minimum in the potential energy both for the assumed conformation and for the intramolecular hydrogen bonding. On the other hand, other conformations may be present in solution, depending upon concentration and solvent nature, allowing intermolecular hydrogen bonding.

In fact, IR and ^{1}H NMR spectroscopy results (Gullotti *et al.*, 1972) indicated that this is a distinct possibility. However the suggested 'fly-over' structures, implying intramolecular hydrogen bonds between O(1)···N(2) and O(2)···N(1), do not seem very likely. Actually, the existence of such a structure, proposed also for Schiff bases derived from diamines and acetylacetone and formylcamphor, has been criticized by Jensen & Larsen (1977), who claim that there is no evidence for this either in the acetylacetone derivatives (Larsen & Schaumburg, 1971) or in those of formyl-

Table 2. *Comparison of the mean values of the* C—O, N—CH, C—C *bond lengths* (Å) *in free Schiff bases and their metal complexes*

Compound	C—O	N—CH	C—C	Reference
salen H$_2$	1·345 (3)	1·270 (3)	1·456 (4)	a
salph H$_2$	1·345 (6)	1·288 (6)	1·448 (7)	b
Co(salen)	1·305 (7)	1·284 (9)	1·421 (10)	c
Co(salph)	1·298 (5)	1·305 (6)	1·418 (6)	b
Co(salchx)^d	1·321 (16)	1·298 (16)	1·436 (20)	e
M—salen^f	1·321 (3)^g	1·291 (3)^g	1·434 (3)^g	h

(*a*) This work. (*b*) Bresciani Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio (1976). (*c*) Schaefer & Marsh (1969). (*d*) Co^{II} complex of the *meso*-form of *N,N'*-cyclohexylenebis(salicylideneimine). (*e*) Bresciani, Calligaris, Nardin & Randaccio (1974). (*f*) Fe, Co, Cu—salen complexes including different stereochemistries. (*g*) Weighted average values. (*h*) Calligaris, Nardin & Randaccio (1972).

camphor (Jensen & Larsen, 1975). On the other hand, the existence of other conformations has been shown for Me$_2$SnCl$_2$.salen H$_2$ (Randaccio, 1973), where salen H$_2$ is constrained by coordination through its O atoms to assume a nearly *gauche* conformation around the CH$_2$—CH$_2$ bond.

By coordination of transition-metal atoms the salen-type ligands undergo different structural modifications since they can act both as bis-bidentate and quadridentate ligands, in the latter case being able to assume planar and twisted structures (Calligaris, Nardin & Randaccio, 1972). However, the most interesting feature is the variation of the bond lengths between the free and coordinated ligand. Table 2 reports the most significant data relative to the chelating moieties of the molecule; C—C refers to carbon distances adjacent to the N—CH bonds. As already observed in the case of salph derivatives, coordination causes a shortening of the C—O and C—C bond lengths together with a lengthening of the N—CH distances. Data reported in Table 2 show that this trend is well established also for salen complexes and their substitution derivatives. This means that after chelation there is a significant contribution of other resonance forms leading to an extended conjugation in the complex molecules (Bresciani Pahor *et al.*, 1976).

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A Novel Intercalation of a Water Molecule Between Pyrimidine Bases in 5-Nitro-1-(β-D-ribosyluronic acid)—Uracil Monohydrate [1-(5-Nitro-2,4-dioxopyrimidinyl)-β-D-ribofuranuronic Acid Monohydrate]*

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Abstract. $C_9H_9N_3O_9 \cdot H_2O$, monoclinic, $P2_1$, $a = 8 \cdot 982$ (1), $b = 10 \cdot 245$ (1), $c = 6 \cdot 651$ (1) Å, $\beta = 92 \cdot 27$ (1)° at 22 ± 3 °C, $V = 611 \cdot 5$ Å³, $Z = 2$, FW 321, $\lambda(\text{Cu } K\alpha) = 1 \cdot 54051$ Å, D_m (flotation) $= 1 \cdot 74$, $D_x = 1 \cdot 75$ g cm⁻³, $\mu(\text{Cu } K\alpha) = 7 \cdot 6$ cm⁻¹, $R = 0 \cdot 056$. The molecule exhibits *anti* conformation ($\chi_{CN} = 53 \cdot 9$°), an intramolecular $C(6)$—$H \cdots O(5')$ hydrogen bond and $C(2')$-*endo*, $C(3')$-*exo* ($^2T_3$) pucker. Two unusual features in this structure are (*a*) the intercalation of water molecules between stacked pyrimidine rings $6 \cdot 55$ Å apart and related by the c translation and (*b*) a number of C—$H \cdots O$ interactions.

Introduction. In connection with a project on radiation sensitization, we have been investigating a series of nitro-substituted bases and nucleosides. Our interest in these structures was to study the hydrogen-bonding scheme of these modified nucleosides as well as to correlate the orientation of the 'g' tensor of these nitro radicals (analysis in progress by Dr H. Box of this Institute) using spin resonance techniques.

The title compound (I) was first synthesized by Fox and co-workers (Wempen, Doerr, Kaplan & Fox, 1960) in the course of their screening of nitro analogs of nucleosides for possible antitumour activities. Crystals of the title compound were obtained by the addition of conc. HNO_3 to the aqueous solution of uridine, followed by slow evaporation of the resulting solution. The unit-cell and other crystallographic data are given

in the *Abstract*. 1438 reflections (only nine had intensities $<2\sigma$) to the limit of $2\theta = 165°$ for Cu $K\alpha$ were collected using the stationary-crystal–stationary-counter procedure (Furnas & Harker, 1955) and were processed in the usual way. A detailed absorption correction depending on the shape of the crystal (Coppens, 1970) was carried out.

The structure (Fig. 1) was solved by a combination of *MULTAN* (Germain, Main & Woolfson, 1971) and trial-and-error methods. One of the E maps gave two

Table 1. *Atomic coordinates* $(\times 10^4)$ *for the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
O(2)	−9044 (3)	−1340	−2062 (5)
O(4)	−4194 (4)	−314 (4)	−2930 (7)
O(5a)	−3341 (4)	−4313 (4)	−3432 (10)
O(5b)	−2341 (4)	−2420 (4)	−2980 (7)
O(2')	−9866 (4)	−4206 (4)	−5669 (6)
O(3')	−11014 (4)	−6051 (4)	−2972 (7)
O(1')	−8172 (4)	−4886 (3)	−874 (5)
O(5')	−5929 (4)	−6404 (4)	−2014 (7)
O(5")	−7240 (4)	−8221 (4)	−1602 (8)
OW	−6568 (4)	−2662 (4)	−7914 (7)
N(1)	−7450 (4)	−3033 (3)	−2631 (6)
N(3)	−6599 (4)	−886 (4)	−2476 (7)
N(C5)	−3429 (4)	−3132 (5)	−3147 (7)
C(2)	−7795 (5)	−1717 (4)	−2357 (7)
C(4)	−5118 (5)	−1182 (5)	−2781 (7)
C(5)	−4888 (4)	−2585 (5)	−2940 (7)
C(6)	−6043 (5)	−3426 (5)	−2863 (7)
C(1')	−8635 (4)	−4028 (4)	−2458 (7)
C(2')	−8891 (5)	−4868 (4)	−4302 (7)
C(3')	−9479 (4)	−6124 (4)	−3402 (7)
C(4')	−8545 (5)	−6215 (4)	−1449 (7)
C(5')	−7151 (5)	−7047 (4)	−1715 (7)