Acta Cryst. (1997). C**53**, 1351–1354

A Hydrated Schiff Base Derivative of Bis(acetylacetone)ethylenediimine with 2-Pyridinylethyl Side Chains

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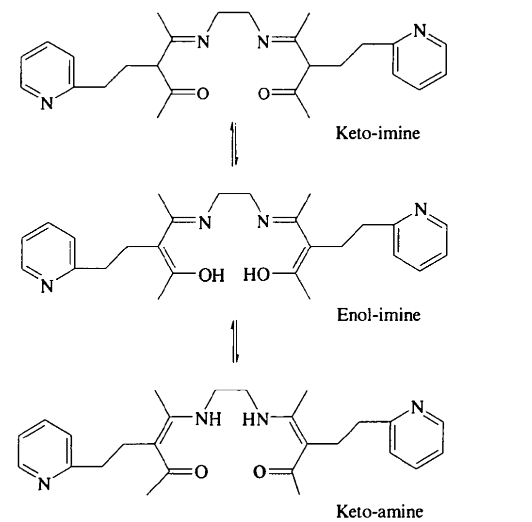
(*Received 20 September 1996; accepted 3 April 1997*)

Abstract

3,10-Bis[2-(2-pyridinyl)ethyl]-4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione tetrahydrate, $C_{26}H_{34}N_4O_2.4H_2O$, exists as a keto–amine tautomer, *i.e.* the 3,9-diene. There are two independent molecules in the triclinic unit cell, each located on a crystallographic inversion center. The orientation of the pyridine rings creates a pseudo-inversion center midway between the molecular centers. Eight water molecules are also present in the unit cell.

Comment

The title compound,† hereafter Ddddd, is a Schiff base compound prepared from one mole of ethylenediamine and two moles of the diketone 3-[2-(2-pyridinyl)ethyl]-2,4-pentanedione. Ddddd is a derivative of the well known Schiff base 4,9-dimethyl-5,8-diazadodeca-4,8-diene-2,11-dione, more commonly known as bis(acetylacetone)ethylenediimine and abbreviated as H_2baen. Compounds of this type can exist in three tautomeric forms (see scheme below), *i.e.* a non-hydrogen-bonded keto–imine, a hydrogen-bonded enol–imine and a hydrogen-bonded keto–amine. It has been shown by IR and H NMR evidence that in the solid state and in most common organic solvents H_2baen exists completely as the hydrogen-bonded tautomers with at least 80% contribution from the keto–amine form (Ueno & Martell, 1955; Dudek & Holm, 1961). Similar conclusions have been drawn for Ddddd (Nathan, Balzer, Larsen & Casalnuovo, 1993) based on the following evidence: (i) the C=O stretch at 1593 cm^{-1} occurs at a frequency lower than that expected of a free carbonyl (about 1700 cm^{-1}) due to conjugation and hydrogen bonding; (ii) a broad medium-intensity IR absorption band occurs at about 3045 cm^{-1} due to hydrogen-bonded O—H or N—H groups; (iii) a strong IR absorption at 1290 cm^{-1} is consistent with the presence of an O—H group in a hydrogen-bonded ring system; (iv) there is no H NMR resonance attributable to the methine H atoms of the keto–imine tautomer; and (v) the H NMR resonance for the ethylenediamine CH_2 groups (at δ 3.42) is not a singlet as expected, but rather is a multiplet due to spin–spin coupling with the amine H atom present in the keto–amine tautomer. It was of interest to compare the structural features of Ddddd implied by the spectral data with that actually existing in crystalline form.



There are two independent Schiff base molecules (Figs. 1 and 2; Table 1) and eight water molecules in the triclinic unit cell. Each molecule is located on a crystallographic inversion center (at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and $0,\frac{1}{2},\frac{1}{2}$). There is a pseudo-inversion center between the molecules (at $\frac{1}{4},\frac{1}{2},\frac{1}{2}$). This is not a true inversion center because one of the pyridine rings is flipped over relative to the other (Fig. 1). Refinements performed on all four permutations of the pyridine-ring orientations confirm the sole orientation shown in Fig. 1.

The absence of the keto–imine tautomer is confirmed by (i) the 120° bond angles about C4 and C4′, and (ii) the planarity of the C3/C4/C5/C7 and C3′/C4′/C5′/C7′ units, where atomic displacements (in Å) from the best least-squares planes are: C3 −0.001 (1), C4 0.002 (2), C5 −0.001 (1), C7 −0.001 (1), C3′ 0.001 (1), C4′ −0.004 (1), C5′ 0.001 (1) and C7′ 0.001 (1).

The sole presence of the keto–amine tautomer is demonstrated by (i) the presence of HN1 and HN1′ (*via* difference Fourier maps) with N—H bond lengths of 0.78 (7) and 0.89 (7) Å, respectively, and (ii) the C5—O1, C5′—O1′, O1···HN1 and O1′···HN1′ distances of 1.265 (4), 1.272 (4), 1.92 (3) and 1.89 (3) Å, respectively, all of which are typical of hydrogen-bonded C=O groups.

† Compounds of this type are named conventionally as the non-hydrogen-bonded keto–imine tautomers. The keto–amine tautomer found is a 3,9-diene. CAS nomenclature for this compound, 4,4′-(1,2-ethanediyldinitrilo)bis{3-[2-(2-pyridinyl)ethyl]}-2-pentanone, is also based on the non-hydrogen-bonded keto–imine tautomer.

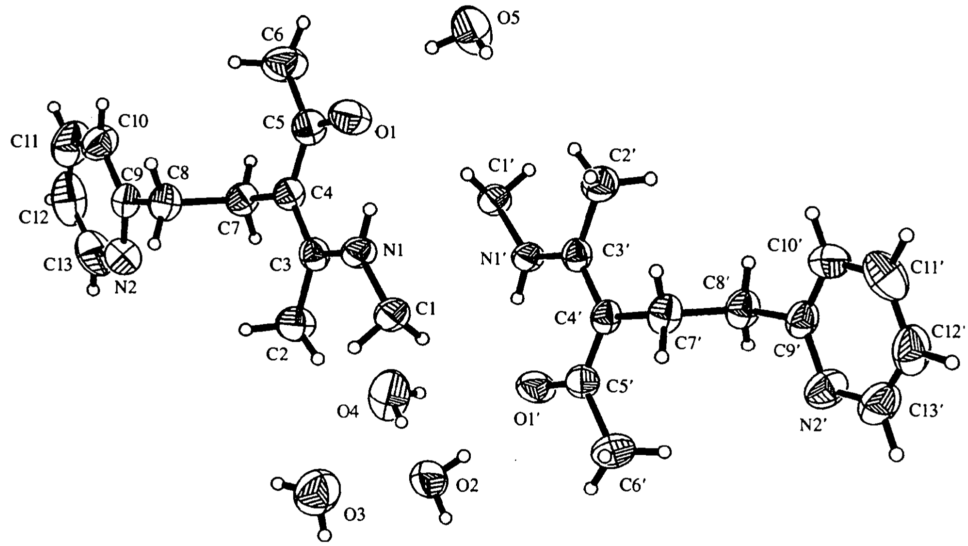


Fig. 1. *ORTEP* drawing showing the asymmetric unit and the atom-numbering scheme. Ellipsoids represent the 50% probability level for the non-H atoms.

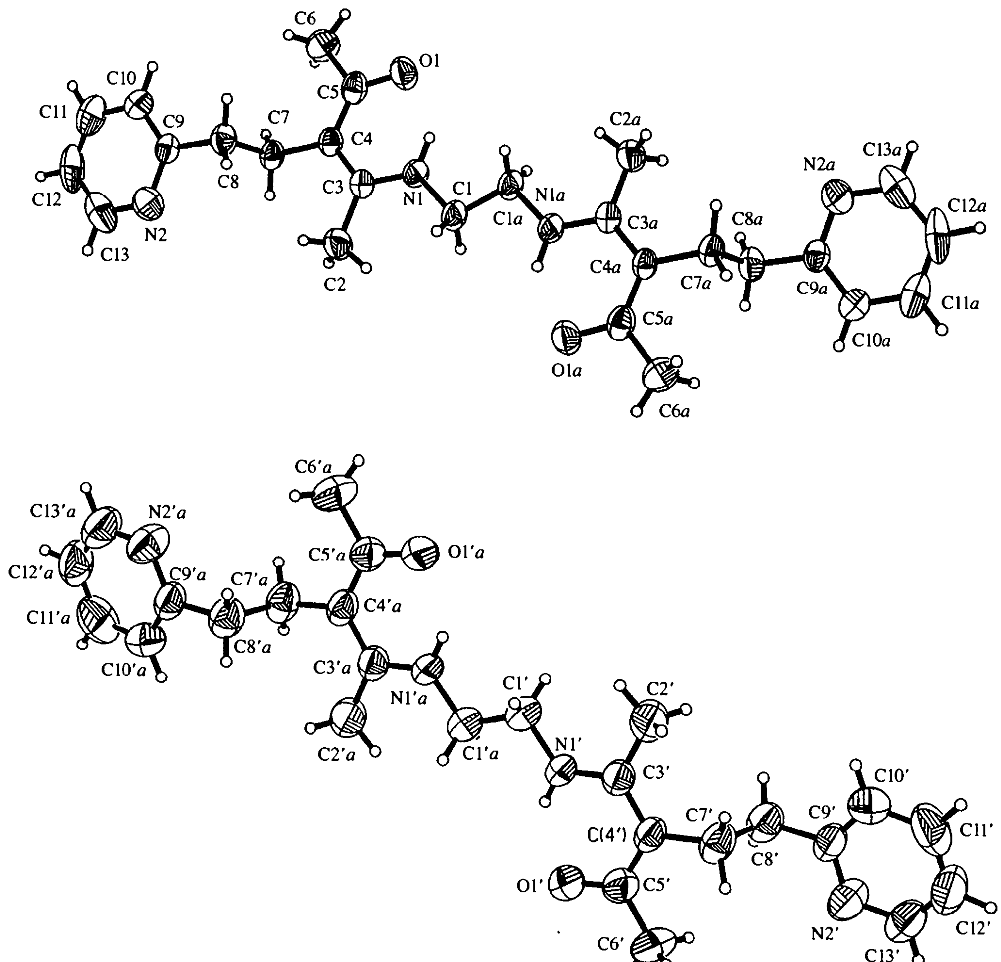


Fig. 2. *ORTEP* drawings of the two independent Ddddd molecules. Ellipsoids represent the 50% probability level for the non-H atoms. [Symmetry code: (*a*) $1-x, 1-y, 1-z$].

Two of the four water molecules in the asymmetric unit appear to be hydrogen-bonded to the Schiff base molecules. The HO5*A*···O1 and HO2*A*···O1′ distances are 2.01 and 1.93 Å, respectively. The other two water molecules appear to be lattice water, perhaps resulting from crystal growth in incompletely dried benzene.

Experimental

The compound Ddddd was prepared *via* a two-step synthesis as described previously (Nathan *et al.*, 1993) and recrystallized from benzene yielding white needles, m.p. 407–409 K. Crystals were grown from dichloromethane/benzene.

Crystal data

$C_{26}H_{34}N_4O_2.4H_2O$
M_r = 506.64
Triclinic
$P\bar{1}$
a = 9.465 (2) Å
b = 10.505 (2) Å
c = 15.797 (3) Å
α = 70.63 (3)°
β = 83.13 (3)°
γ = 69.87 (3)°
V = 1391.2 (5) $Å^3$
Z = 2
D_x = 1.209 Mg m^{-3}
D_m = 1.17 Mg m^{-3}
D_m measured by flotation in benzene/CCl_4
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 38 reflections
θ = 16–21°
μ = 0.086 mm^{-1}
T = 293 K
Needle
0.64 × 0.24 × 0.13 mm
White

Data collection

Automated Picker four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5033 measured reflections
4903 independent reflections
2215 reflections with $I > 2\sigma(I)$
R_{int} = 0.009
θ_{max} = 25°
$h = 0 \rightarrow 12$
$k = -16 \rightarrow 18$
$l = -11 \rightarrow 10$
4 standard reflections every 400 reflections intensity decay: 1.05%

Refinement

Refinement on F^2
R = 0.067
wR = 0.177
S = 1.273
4895 reflections
331 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max}$ = 0.29 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.27 e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C5	1.265 (4)	O1′—C5′	1.272 (4)
N1—C3	1.335 (4)	N1′—C3′	1.322 (4)
N1—C1	1.448 (3)	N1′—C1′	1.455 (3)
N2—C13	1.348 (4)	N2′—C13′	1.338 (4)
N2—C9	1.350 (4)	N2′—C9′	1.349 (4)
C1—C1*a*	1.499 (5)	C1′—C1′*a*	1.506 (5)
C2—C3	1.495 (4)	C2′—C3′	1.496 (4)
C3—C4	1.405 (4)	C3′—C4′	1.398 (4)
C4—C5	1.415 (4)	C4′—C5′	1.418 (4)
C4—C7	1.514 (4)	C4′—C7′	1.516 (4)
C5—C6	1.502 (4)	C5′—C6′	1.508 (4)
C7—C8	1.537 (4)	C7′—C8′	1.535 (4)
C8—C9	1.492 (4)	C8′—C9′	1.503 (4)
C9—C10	1.374 (4)	C9′—C10′	1.364 (4)
C10—C11	1.358 (5)	C10′—C11′	1.392 (5)
C11—C12	1.345 (5)	C11′—C12′	1.368 (5)
C12—C13	1.382 (5)	C12′—C13′	1.342 (5)
N1—HN1	0.78 (7)	N1′—HN1′	0.89 (7)
N1—C3—C4	121.3 (3)	N1′—C3′—C4′	121.9 (3)
N1—C3—C2	116.5 (3)	N1′—C3′—C2′	116.7 (3)
C4—C3—C2	122.2 (3)	C4′—C3′—C2′	121.4 (3)
C3—C4—C5	120.8 (3)	C3′—C4′—C5′	120.5 (3)
C3—C4—C7	119.7 (3)	C3′—C4′—C7′	120.4 (3)
C5—C4—C7	119.5 (3)	C5′—C4′—C7′	119.0 (3)
O1—C5—C4	122.8 (3)	O1′—C5′—C4′	123.2 (3)
O1—C5—C6	116.3 (3)	O1′—C5′—C6′	115.5 (3)
C4—C5—C6	120.9 (3)	C4′—C5′—C6′	121.3 (3)

Symmetry code: (*a*) $1 - x, 1 - y, 1 - z$.

Refinement was successful in the triclinic space group $P\bar{1}$. Transformation to a metrically acceptable C-centered monoclinic cell was rejected on the basis of merging statistics; R_{int} = 0.650 for 2383 pairs of potentially equivalent reflections.

Of the 4903 unique reflections, less than half (2215) were observed with the criterion $I > 2\sigma(I)$. The orientation of the pyridine rings creates a pseudo-inversion center midway between the molecular centers. Since one molecule is thereby offset from the other by a translation of ($\frac{1}{2}$,0,0), a pseudo-systematic absence of *hkl*, $h = 2n + 1$, is observed, which, in turn, results in approximately half of the data being extremely weak. Because of the large number of weak reflections, refinement was performed on F^2 using all of the data.

H atoms on the pyridine rings and carbon chains were added at ideal positions. H atoms on the water molecules and amine N atoms were located from difference Fourier maps and improved to ideal positions. No H atoms were observed near the keto O atoms O1 and O1′. Displacement parameters were calculated from U_{eq} of the atoms to which H atoms are bonded (nU_{eq} where n was 1.5 for CH, CH_3, H_2O, and NH groups, and 1.2 for CH_2 groups). Although refinements were performed using the riding hydrogen model, in the last cycles, the positional parameters for the two amine H atoms, HN1 and HN1′, were allowed to refine in order to better identify the tautomer(s).

Because pseudo-symmetry is a key factor in the solution of this structure, four permutations of the pyridine ring orientations (namely, as shown in Fig. 1, with N2 and C10—H10 interchanged, with N2′ and C10′—H10′ interchanged, and with both sets of atoms interchanged) were subjected to refinement, yielding final R values of 0.0666, 0.0734, 0.0740 and 0.0767, respectively.

Data collection: *PCPS* (*XTEL* Program Library†). Cell refinement: *QACELL* (*XTEL*†). Data reduction: *PREF*, *DATPRO1*, *SORTU*, *DATPRO2* (*XTEL*†). Program(s) used to solve structure: *SHELXTL4*.20 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL5*.03 (Sheldrick, 1994). Molecular graphics: *SHELXTL5.03*/*ORTEP*. Software used to prepare material for publication: *SHELXTL5*.03.

† The *XTEL* Program Library used by the Indiana University Molecular Structure Center consists of a series of mostly public domain programs which have been obtained from various sources.

The authors gratefully acknowledge assistance from the Indiana University Molecular Structure Center.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1293). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1354–1356

6,6-Diphenylfulvene at 140 K

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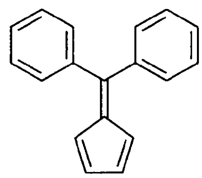
(*Received 27 February 1997; accepted 17 April 1997*)

Abstract

The title compound, $C_{18}H_{14}$, crystallizes with two molecules in the asymmetric unit, which differ only in the angle between the phenyl rings and the fulvene moiety. The two double bonds of the cyclopentadiene moiety are shortened [1.352 (2) and 1.353 (2) Å] in the title compound compared with the range found in its metal complexes (1.381–1.520 Å). The bond joining these two double bonds is generally shorter in the metal complexes than in the title compound [1.467 (2) and 1.468 (2) Å], but there are exceptions. A conformational analysis of the title compound with the molecular modelling program *MOMO* [Bolte, Beck & Egert (1991). *Molecular Modelling Program MOMO*. University of Frankfurt, Germany] shows only one minimum on the energy hypersurface, where both phenyl rings form an angle of 56.6° with the fulvene moiety.

Comment

Crystallographic information about 6,6-diphenylfulvene, (I), as retrieved from the Cambridge Structural Database (Allen & Kennard, 1993), is so far only available for structures where the molecule acts as a ligand for various metal atoms. In all cases, at least one of the fulvene double bonds, but never a phenyl ring, complexes the metal atom.



(I)

We have determined the crystal structure of (I), which crystallizes with two independent but very similar molecules in the asymmetric unit, in order to compare it with those where the fulvene moiety acts as a ligand to Ni ($C_{26}H_{26}Ni$: Edelmann, Lubke & Behrens, 1982), Fe ($C_{21}H_{14}O_3Fe$: Edelmann, Lubke & Behrens, 1982; $C_{26}H_{14}O_8Fe_2$: Behrens, 1976), Pt ($C_{61}H_{52}P_2Pt$: Christofides, Howard, Spencer & Stone, 1982), Co ($C_{23}H_{19}Co$: Wadepohl & Pritzkow, 1991) and

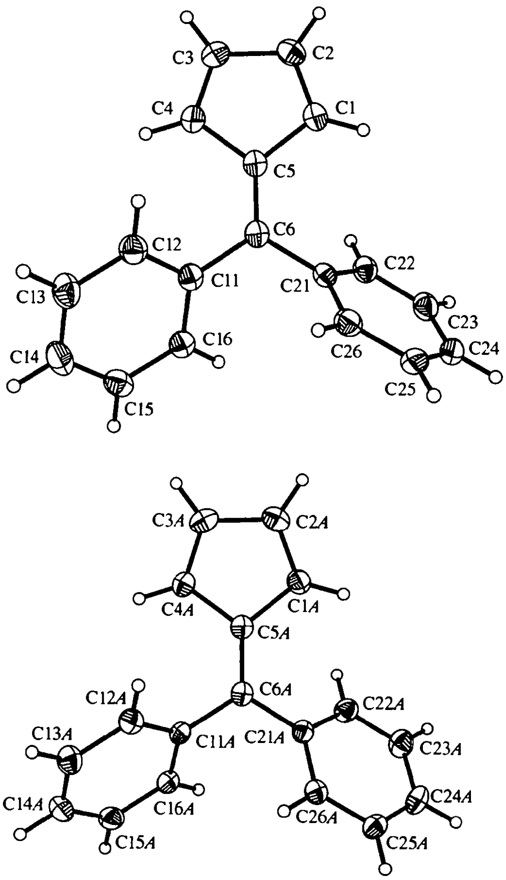


Fig. 1. A perspective view (not the relative orientation in the crystal) of the independent molecules of the title compound with the atom-numbering scheme; displacement ellipsoids are at the 50% probability level.