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N,*N*′-Ethylenebis(acetylacetoneimine)

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Abstract. $C_{12}H_{20}N_2O_2$, $M_r = 224{\cdot}3$, triclinic, $P\bar{1}$, $a = 7{\cdot}173\,(8)$, $b = 10{\cdot}50\,(1)$, $c = 13{\cdot}46\,(1)$ Å, $\alpha = 108{\cdot}9\,(1)$, $\beta = 125{\cdot}4\,(1)$, $\gamma = 101{\cdot}0\,(1)°$; $U = 680{\cdot}5$ Å^3; $D_m = 1{\cdot}11$, $D_c = 1{\cdot}09$ Mg m^{-3}, $Z = 2$; $\mu = 0{\cdot}081$ mm^{-1} (Mo $K\alpha$); $F(000) = 244$. Direct methods were used to determine the structure from three-dimensional X-ray data. Block-diagonal-matrix least-squares refinement, based on 1422 independent reflections, converged with R at 0·054. Crystals are built up of discrete molecules characterized by a conjugated enaminoketone structure and intramolecular hydrogen bonds. The molecule as a whole has approximate 2 (C_2) symmetry.

Introduction. Intensity data were collected on a Siemens diffractometer by the θ–2θ scan technique with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). 1422 independent reflections with $I > 3\sigma(I)$ were measured up to $2\theta = 52°$ and corrected for the Lorentz and polarization effects. No corrections for absorption ($\mu R = 0{\cdot}02$) or extinction were applied. The scattering factors were those of Moore (1963). The structure was solved by direct methods using the routine for centrosymmetric structures of the *SHELX* system (Sheldrick, 1976). The E maps, computed with the third most consistent set of signs, revealed all the non-hydrogen atoms of the molecule. For subsequent calculations programs written by Albano, Domenicano & Vaciago (1966) were used. After anisotropic block-diagonal-matrix least-squares refinement, a difference Fourier synthesis was calculated in order to locate the H atoms. Two peaks appeared to correspond to H atoms bonded to N atoms, while no positive electron density was found near the O atoms. In the final refinement, only the two iminic H atoms were allowed to vary, the contributions of the others being held constant ($B = 5$ Å^2) at calculated positions. The R factor was reduced to 0·054, using the weighting scheme $w = 1/(A + |F_o| + B|F_o|^2)$ where A ($= 1{\cdot}90$) and B ($= 0{\cdot}0125$) were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and ($\sin\theta/\lambda$). Final atomic parameters are listed in Table 1* together with their estimated standard deviations calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering scheme of the atoms is shown in Fig. 1.

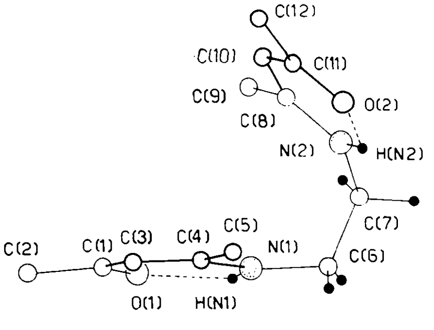

Fig. 1. A view of the molecule with the atom-numbering scheme.

Discussion. The structures of some Schiff bases in solution, formed by condensation of β-diketones and -diamines, have been investigated by ^{1}H NMR, absorption and circular dichroism spectroscopy, which gave useful information about tautomeric equilibria and hydrogen bonding as well as some indication of the predominant conformation (Gullotti, Pasini, Fantucci, Ugo & Gillard, 1972; Jensen & Larsen, 1975, 1977).

The crystal structure determinations of Schiff bases are of interest for a better understanding of their molecular structures, necessary for the correct interpretation of their properties in solution. Furthermore, the comparison of accurate structural parameters of the free ligands with those of their metal complexes allows a discussion of the bonding nature in the metal complexes and hence a rationalization of some of their properties (Calligaris, Nardin & Randaccio, 1972).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Suplementary Publication No. SUP 34598 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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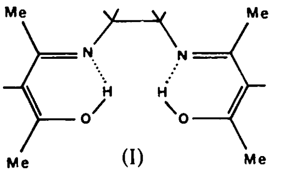
Table 1. *Fractional coordinates* (×10⁴) *with estimated standard deviations in parentheses*

H atoms are numbered according to the atom to which they are bonded which is given by the first number in parentheses. The isotropic temperature factors of the two minimized hydrogen atoms, H(N1) and H(N2), are 4·4 (9) and 5·1 (1·1) Å², respectively.

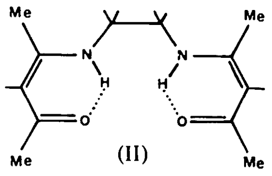
	x	*y*	*z*
O(1)	5046 (3)	3460 (2)	4719 (1)
O(2)	3301 (3)	3146 (2)	−1160 (1)
N(1)	6125 (3)	4855 (2)	3590 (2)
N(2)	2419 (3)	4247 (2)	574 (2)
C(1)	5920 (4)	2649 (3)	4422 (2)
C(2)	6205 (5)	1523 (3)	4902 (3)
C(3)	6742 (4)	2744 (3)	3681 (2)
C(4)	6839 (4)	3821 (3)	3295 (2)
C(5)	7839 (4)	3820 (3)	2549 (2)
C(6)	6101 (4)	6034 (3)	3237 (2)
C(7)	3365 (4)	5563 (3)	1884 (2)
C(8)	931 (4)	2761 (3)	−19 (2)
C(9)	−440 (5)	2345 (4)	465 (3)
C(10)	582 (5)	1589 (3)	−1076 (2)
C(11)	1872 (5)	1850 (3)	−1560 (2)
C(12)	1493 (6)	447 (4)	−2626 (3)
H(N1)	5571 (50)	4816 (34)	4133 (27)
H(N2)	3414 (59)	4481 (40)	329 (31)
H(21)	6972	956	4608
H(22)	4440	728	4413
H(23)	7394	2075	5973
H(3)	7309	1990	3430
H(51)	8369	3004	2455
H(52)	9424	4859	3169
H(53)	6448	3621	1577
H(61)	6797	7036	4092
H(62)	7301	6223	3074
H(71)	2119	5271	2009
H(72)	3390	6475	1778
H(91)	−1496	1169	−97
H(92)	−1645	2769	263
H(93)	898	2742	1522
H(10)	−670	479	−1546
H(121)	290	−538	−2861
H(122)	3206	478	−2194
H(123)	648	399	−3550

So far X-ray analyses of free tetradentate Schiff bases have been carried out only in a few cases (Bresciani-Pahor, Calligaris, Delise, Dodic, Nardin & Randaccio, 1976; Bresciani-Pahor, Calligaris, Nardin & Randaccio, 1978; Jensen, Kristensen, Mosbaek & Søtofte, 1978). Here we present the crystal and molecular structure of the condensation product between one molecule of 1,2-ethylenediamine and two molecules of acetylacetone: *N*,*N*′-ethylenebis(acetylacetoneimine), hereinafter en(acacH)$_2$.

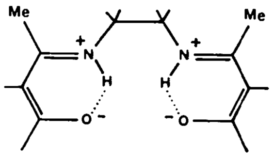
The X-ray-analysis results show that the crystal consists of discrete molecules characterized by an enaminoketone structure and intramolecular hydrogen bonding (Fig. 1), as was found in solution from NMR (Dudek & Holm, 1969; Gullotti *et al.*, 1972). Thus of the two possible structures, (I) and (II), the former can be ruled out.



(I)



(II)



(III)

However, inspection of bond lengths and angles (Table 2) shows that there is a certain amount of conjugation within the enaminoketone groups, suggesting resonance resulting in ionic structures such as (III). In fact the mean value of the N—C(sp^2) distances of 1·331 Å is about 0·12 Å shorter than that expected for a single N—C(sp^2) bond, while the C—C distances within the rings (mean values, 1·393 and 1·440 Å) are indicative of a different amount of π bonding.

Similarly the C—O bond lengths (mean, 1·243 Å) are slightly longer than expected for pure C=O double bonds, and very close to those found in amides and peptides (*Molecular Structures and Dimensions*, 1972). The existence of delocalization is further supported by the trigonal geometry of the N atoms, as shown by the sums of their bond angles which are close to 360°. Thus the two chemically equivalent halves of the molecule are nearly planar within ±0·005 and ±0·006 Å respectively, and, as a consequence of free rotation around the single N—CH$_2$ and CH$_2$—CH$_2$ bonds, they make a dihedral angle of 41°. The torsion angles

Table 2. *Bond lengths* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

C(1)–O(1)	1·245 (4)	C(8)–N(2)	1·333 (3)
C(1)–C(2)	1·514 (5)	C(8)–C(9)	1·532 (6)
C(1)–C(3)	1·441 (5)	C(8)–C(10)	1·391 (4)
C(3)–C(4)	1·395 (5)	C(10)–C(11)	1·440 (6)
C(4)–C(5)	1·536 (5)	C(11)–C(12)	1·525 (5)
C(4)–N(1)	1·329 (3)	C(11)–O(2)	1·242 (4)
C(6)–N(1)	1·462 (4)	N(1)–H(1)	1·02 (4)
C(6)–C(7)	1·521 (3)	N(2)–H(2)	0·97 (5)
C(7)–N(2)	1·467 (3)		

C(6)–N(1)–H(1)	117·9 (2·2)	O(1)–C(1)–C(2)	118·1 (3)
C(6)–C(7)–N(2)	111·6 (3)	O(1)–C(1)–C(3)	124·0 (3)
C(7)–N(2)–C(8)	125·9 (3)	C(2)–C(1)–C(3)	117·9 (3)
C(7)–N(2)–H(2)	113·7 (1·7)	C(1)–C(3)–C(4)	124·7 (3)
C(8)–N(2)–H(2)	117·5 (2·1)	C(3)–C(4)–C(5)	119·1 (3)
N(2)–C(8)–C(9)	119·1 (3)	C(3)–C(4)–N(1)	120·8 (3)
N(2)–C(8)–C(10)	121·2 (3)	C(5)–C(4)–N(1)	120·2 (3)
C(9)–C(8)–C(10)	119·7 (3)	C(4)–N(1)–C(6)	126·6 (3)
C(8)–C(10)–C(11)	124·2 (3)	C(4)–N(1)–H(1)	115·5 (2·2)
C(10)–C(11)–C(12)	118·2 (3)	N(1)–C(6)–C(7)	112·4 (2)
C(10)–C(11)–O(2)	124·5 (3)		
C(12)–C(11)–O(2)	117·2 (4)		

Table 3. *Comparison of the mean values of the* C–O, C–N *and* C–C *bond lengths* (Å) (*see Fig.* 1 *for numbering scheme*) *in free acetylacetone Schiff bases and their metal complexes*

Except for the last row of figures, the e.s.d.'s are the means of the individual values.

Compound	C(1)–O(1)	C(4)–N(1)	C(1)–C(3)	C(3)–C(4)
en(acacH)$_2$[a]	1·243 (4)	1·331 (3)	1·440 (5)	1·393 (5)
K[Coen(acac)$_2$gly].2H$_2$O[b]	1·300 (4)	1·306 (5)	1·367 (6)	1·416 (6)
Coen(acac)$_2$N$_3$py[c]	1·274 (7)	1·293 (8)	1·382 (9)	1·406 (9)
*M*en(acac)$_2$[d]	1·294 (3)	1·308 (4)	1·366 (5)	1·423 (6)

(*a*) This work. (*b*) Holbrook & van der Helm (1975). (*c*) Clearfield, Gopal, Kline, Sipski & Urban (1978). (*d*) VO,Cu,Co complexes with different stereochemistries, reported distances are weighted average values of 15 series of bond lengths (Calligaris *et al.*, 1972).

around the N(1)–C(6), N(2)–C(7) and C(6)–C(7) bonds are respectively 94·1, 100·0, −67·2°, according to the sign convention recommended by Klyne & Prelog (1960).

Therefore the molecule possesses an approximate 2 (C_2) symmetry, the twofold axis passing through the midpoints of the C(6)–C(7) and N(1)–N(2) segments. An analogous approximate symmetry and bond-length trend has been found in the cyclohexanediimine-thio derivative (Jensen *et al.*, 1978) where, however, the torsion angles around the N–C bonds are larger (137·3 and 155·2°), while that around the single C–C bond is −62·3°. Also energy calculations based on a simplified force field (Calligaris, 1979) suggest the possibility of other geometries corresponding to *gauche* and *trans* conformations of the ethylene bridge. It seems likely that the structure found in the solid state is stabilized by packing forces.

However, the 'fly-over' structure proposed by Gullotti *et al.* (1972) for this kind of Schiff base, that is a structure with crossed intramolecular hydrogen bonds, does not seem acceptable since it should result in a dramatically hindered structure if the acetylacetoneimine residues are to remain planar.

In en(acac)$_2$ metal complexes, an increase in the C–O bond lengths (mean, 1·293 Å) and a decrease in the C–N distances (mean, 1·307 Å), with a parallel rearrangement of the C–C distances, is observed (Table 3). Similar variations have been observed previously for tetradentate Schiff bases containing salicylaldehyde and their metal complexes, but in opposite directions since such ligands exist in the enoliminic form both in solution and in the solid state (Bresciani-Pahor *et al.*, 1978). Such a trend in the bond lengths may be expected for the dianionic form of the ligand. On the other hand the transition-metal atom itself can further influence the conjugation through interaction of its *d* electrons with the ligand *π* orbitals, as already suggested on the basis of the coordination bond lengths (Calligaris *et al.*, 1972).

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