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Synthesis and Crystal Structure of the Hydrogen Bonded Molecular Self-complex of *N*-(2,2-Diacetylvinyl)-*o*-phenylenediamine

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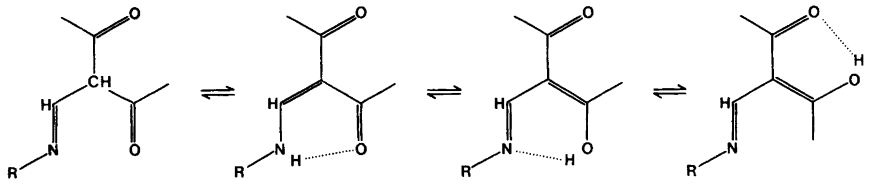
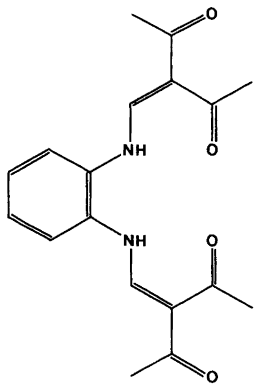
The yellow title compound ($C_{12}H_{14}N_2O_2$) crystallizes with four molecules in a monoclinic unit cell with dimensions $a=10.259(2)$ Å, $b=10.988(3)$ Å, $c=10.896(2)$ Å, $\beta=114.17(1)°$. The space group is $P2_1/c$. The structure was solved by direct methods and refined by the method of least-squares. The final $R=0.036$ for 1738 observed reflections. The tautomer in the crystal is the enamine stabilized by a short intramolecular NH···O hydrogen bond as part of a six-membered ring. The N···O distance is 2.596(3) Å. The azomethino pentane-2,4-dione part is approximately planar, and the molecules form pairs where these parts are overlapped with interplanar distances of 3.45 Å. This self-complex is further strengthened by weak intermolecular hydrogen bonds between the amino groups and carbonyl oxygens.

During the last decade much interest has been focused on the electrocatalytical properties of macrocyclic planar MN_4 chelates of cobalt and iron, *e.q.* phtalocyanins and cobalt dibenzotetraazaannulene.[1] The latter substance has good cata-



1a 1b 1c 1d



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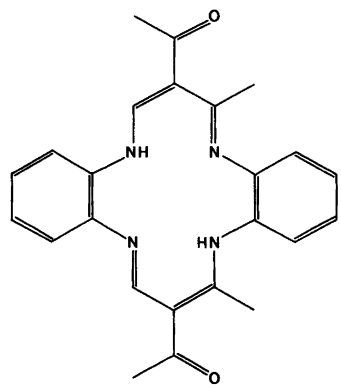

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lytical properties but since it is difficult to synthesize in large quantities the electrocatalytical activity of other chelates of Co and Fe has been investigated.[2]

Attempts to condense 1,2-bis(3-azomethinopentane-2,4-dione)benzene (*2*) with 1,2-diaminobenzene did not lead to the anticipated tetraaza macrocycle (*3*) but to the title compound (*1*). This compound has some interesting properties. It was shown to be versatile both in chelating with cations,[3] as a terdentate ligand, as well as undergoing reactions in aqueous acid solution.[4] The structure determination of (*1*) which is the subject of this paper was performed to throw light on these properties and to study the tautomerism of an azomethino-β-diketone.

The composition of the equilibrium mixture of the keto-enol tautomerism in β-diketones is dependent *i.a.* on the substituents present in the molecules. Thus for example acetylacetone exists to 80 % in the intramolecularly OH···O bonded enol form while the exchange of one methyl for a carbethoxy group results in an equilibrium composition of just 7.5 % enol form.[5] The ketimine–enamine tautomerism was found long ago[6] to be shifted toward the enamine and similarly the amide–iminol tautomeric equilibrium is normally displaced toward the amide form.[7] In these compounds the C–N bonds have a considerable double bond character nevertheless, and for N···O hydrogen bonds, which are operative, there is a general preference for NH···O bonds. In the system reported here several tautomers are feasible. Four of them are shown (*1*a–d) of which *1*b–d have possibilities of forming intramolecular N···O or O···O hydrogen bonds as part of a six-membered ring.

EXPERIMENTAL

Synthesis. A mixture of 1,2-bis(3-azomethinopentane-2,4-dione)-benzene (*2*)[8] (3.3 g, 0.010 mol) and 1,2-diaminobenzene (1.2 g, 0.011 mol) in 60–70 ml toluene was refluxed for 20–25 mins. The yellow hot solution was then filtered. Yellow crystals started crystallizing from the filtrate in a few minutes. After standing for 24 h at room temperature they were filtered off. The title compound (*1*) was obtained practically pure in 90 % (3.9 g, 0.018 mol) yield, m.p. 170–171 °C. Anal. Calc. for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.46; N, 12.83; O, 14.66 %. Found: C, 65.9; H, 6.49; N, 12.75; O, 14.89 %. ^{1}H NMR (DMSO-d_6): δ 2.40 [d, 6, (-CH_3)], 5.00 [s, 2, (-NH_2)], 7.33 [m, 4, (benzene)], 8.33 [d, 1, J=6 Hz, (-N=CH-)], 12.47 [d, 1, J=6 Hz, (NH···O)]. MS: *m/e* 218 15 %, 119 100 % (M – acetylacetonyl).

X-Ray study. The lustrous crystals of the title compound are platelets with (100) as the principal face. A crystal with approximate dimensions 0.19 × 0.31 × 0.38 mm^3 was mounted on a glass fibre. Integrated intensity measurements were made on a computer-controlled Enraf-Nonius CAD4 diffractometer using Ni-filtered Cu$K\alpha$ radiation. All reflections within a quarter sphere of reciprocal space with radius $(\sin\theta/\lambda) \leq 0.61$ Å^{-1}, were sampled by the $\omega-2\theta$ scan technique with $\Delta\omega = 0.9° + 0.3° \tan\theta$. The maximum time spent on a reflection was 90 s, resulting in a counting statistics precision about 3 %. Three standard reflections were remeasured every other hour. No significant variation in intensity as a function of exposure time was detected. From the observed data the following systematic absences were derived: *h0l* for *l* odd and *0k0* for *k* odd. Two strong reflections of type *h0l*, 501 and 403, could be shown to originate from the Renninger effect by later remeasurement at varying azimuthal angles. The remaining 2140 independent reflections were corrected for Lorentz, polarization and absorption effects. The transmission factors were in the range 0.80 to 0.88. At the later stages of structure refinement an isotropic extinction correction[9] was applied, resulting in $g = 0.49(8) \times 10^3$. Only one percent of the structure amplitudes were corrected by more than one percent, with a maximum correction of 10 % for *F*(211).

Determination and refinement of the structure. The structure was solved using the MULTAN program.[10] After refinement of all the heavy atom positions, an electron density difference map revealed the hydrogen atoms. In the final refinement cycles, all carbon, nitrogen and oxygen atoms were assigned anisotropic temperature factors and the hydrogen atoms isotropic temperature factors. A total of 202 parameters were refined, with 1738 observed structure amplitudes having $I_{obs} > 3\sigma_c(I_{obs})$. The weights used in the least-squares calculations were derived from $w_i^{-1} = \sigma_c^2(F_{obs}) + (0.01|F_{obs}|)^2 + 0.1$, where $\sigma_c(Fobs)$ is the standard deviation due to counting statistics. The resulting agreement indicators are $R = 0.036$, $R_w = 0.041$ and $S = 1.19$.

The final atomic position coordinates and isotropic temperature factor coefficients are given in Table 1. The final anisotropic temperature factor coefficients for carbon, nitrogen and oxygen and the magnitudes of the 1738 observed and calculated structure factors are available on request.

CRYSTAL DATA

N-(2,2-diacetylvinyl)-*o*-phenylenediamine $C_{12}H_{14}N_2O_2$, M = 218.25 g mol^{-1}; m.p. 444 K, mono-

Table 1. Atomic position coordinates and isotropic thermal parameters. The B_{iso} of atoms O(1) to C(12) were derived from the final anisotropic temperature factor coefficients.

Atom	*x*	*y*	*z*	B_{iso}(Å^2)
O(1)	0.48127(16)	0.20339(12)	0.31323(14)	5.2(1)
O(2)	0.26753(14)	−0.09679(10)	0.36790(12)	4.1(1)
N(1)	0.22874(15)	0.02855(12)	0.55185(14)	3.1(1)
N(2)	0.21690(19)	−0.17700(14)	0.69113(17)	3.9(1)
C(1)	0.30250(17)	0.11254(14)	0.52053(16)	2.8(1)
C(2)	0.35108(17)	0.10369(14)	0.41907(15)	2.7(1)
C(3)	0.43368(17)	0.20500(14)	0.39986(16)	3.0(1)
C(4)	0.46223(24)	0.31662(17)	0.48679(21)	3.8(1)
C(5)	0.32068(17)	−0.00680(14)	0.33762(16)	2.9(1)
C(6)	0.35137(35)	−0.01579(22)	0.21441(24)	5.2(1)
C(7)	0.17624(17)	0.03921(14)	0.65329(16)	2.9(1)
C(8)	0.17466(17)	−0.06685(15)	0.72466(17)	3.1(1)
C(9)	0.12412(20)	−0.05684(18)	0.82520(18)	3.8(1)
C(10)	0.07661(20)	0.05301(19)	0.85263(19)	4.1(1)
C(11)	0.07837(20)	0.15666(18)	0.78159(20)	4.0(1)
C(12)	0.12775(19)	0.14880(16)	0.68094(18)	3.4(1)
H(N1)	0.2169(21)	−0.0413(19)	0.5060(21)	5.2(5)
H(N21)	0.2923(24)	−0.1743(19)	0.6705(21)	5.3(5)
H(N22)	0.2194(22)	−0.2404(21)	0.7458(22)	5.7(5)
H(C1)	0.3253(17)	0.1865(15)	0.5756(16)	3.2(4)
H(C4)	0.3762(25)	0.3662(20)	0.4648(22)	5.7(6)
H(C4)	0.4955(24)	0.2985(21)	0.5815(25)	6.2(6)
H(C4)	0.5366(25)	0.3652(22)	0.4756(24)	6.7(6)
H(C6)	0.3147(30)	−0.0866(27)	0.1717(28)	8.7(8)
H(C6)	0.3096(27)	0.0538(24)	0.1562(26)	7.2(7)
H(C6)	0.4559(33)	0.0000(28)	0.2358(30)	10.0(9)
H(C9)	0.1248(20)	−0.1295(18)	0.8747(19)	4.5(4)
H(C10)	0.0405(21)	0.0584(18)	0.9226(21)	5.5(5)
H(C11)	0.0455(19)	0.2331(18)	0.8004(18)	4.3(4)
H(C12)	0.1243(19)	0.2200(17)	0.6265(18)	3.9(4)

clinic, $P2_1/c$, $a=10.259(1)$ Å, $b=10.988(3)$ Å, $c=10.896(1)$ Å, $\beta=114.17(1)°$, $V=1120.5$ Å^3, $D_{calc}=1.294$ g cm^{-3}, $Z=4$, $F(000)=464$, $\mu(CuK\alpha)=7.39$ cm^{-1}.

DISCUSSION

Molecular dimensions. The bond distances and angles are given in Fig. 1. which also shows the atomic numbering used here. The aromatic ring is planar and it is distorted towards C_{2v} symmetry with the twofold axis along the line C(11)−C(8)−N(2). Assuming that the geometrical effects of the substituents on the bond angles and bond lengths of the benzene ring are additive,[11] one can conclude that the amino group N(2)H$_2$ causes most of the ring distortions. The nitrogen atoms deviate slightly [N(1), 0.011(2) Å; N(2), 0.062(2) Å] from the plane of the benzene ring, *cf.* the torsion angles in Table 2. In 1,2-diaminobenzenes the two nitrogen lone pairs are oriented on opposite sides of the aromatic ring plane to maximize the π-interaction.[12,13] The N(2)H$_2$ group has the same conformation as the amino groups of 1,2-diaminobenzene[13] with one NH bond approximately coplanar with the ring, and the C−N bond is short, 1.384(2) Å. The N(1) configuration is trigonal planar: the lone pair has been donated to the N(1)−C(1)−C(2) bonds and there is little π-donation to the aromatic ring. The C(7)−N(1) bond is long, 1.419(2) Å, and furthermore the plane of the phenyl ring is rotated 36.4(2)° out of the plane of the rest of the molecule.

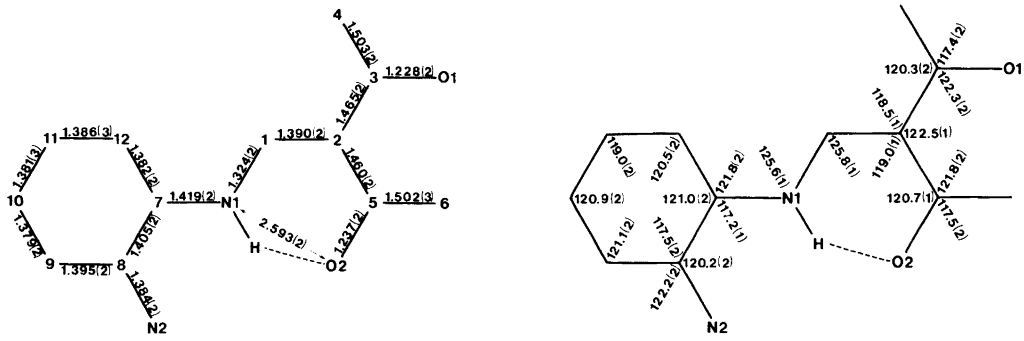

Fig. 1. Bond distances and angles with esd's in parentheses. The atomic numbering used is also shown. The N–H distances are 0.89 to 0.91 Å with esd 0.02 to 0.03 Å. The C–H distances are between 0.96(2) and 1.01(3) Å except one C(6)–H(C6) which is 0.91(2) Å.

Domenicano and Vaciago[14] have pointed out a relation in *e.g.* diphenylaminotriphenylmethane between C(ring)–N torsion angle and distorsions of the endocyclic bond angles: The benzene ring with a C–N torsion of 12.4° is distorted in a manner very similar to that seen in *1* at N(2), but the other ring with a 74.6° torsion angle shows only small bond angle distortions. The observed C(7)–N(1) torsion in the present compound supports the view that the N(2)H_2 group is responsible for the major part of the ring distortions.

Both the bonds N(1)–C(1) and C(1)–C(2) have a high degree of double bond character, the bond lengths being 1.324(2) and 1.390(2) Å, respectively. The non-aromatic part of the molecule approximates to a plane, except for the acetyl group C(6)–C(5)–O(2) which forms an angle of 9.2(2)° to that plane. The non-coplanar orientation of the acetyl group is probably due to the hydrogen bonds accepted by O(2) (*vide infra*).

Table 2. Torsion angles.

Atoms	Angle (°)
N(2)–C(8)–C(7)–N(1)	−2.9(3)
C(8)–C(7)–N(1)–C(1)	−145.0(2)
C(7)–N(1)–C(1)–C(2)	−178.3(2)
N(1)–C(1)–C(2)–C(3)	−178.9(2)
N(1)–C(1)–C(2)–C(5)	−0.2(3)
C(1)–C(2)–C(3)–C(4)	−1.2(3)
C(1)–C(2)–C(3)–O(1)	179.3(2)
C(1)–C(2)–C(5)–C(6)	171.2(2)
C(1)–C(2)–C(5)–O(2)	−8.4(2)

The approximate planarity of the molecule causes crowding shown by the distorsions of the bond angles at the C(2), C(3) and C(5) atoms. Thus for example the C(methyl)–C–O angles are 117.5°

Table 3. Geometry of the hydrogen bonding.

(a) intramolecular	
N(1)···O(2) (Å)	2.593(2)
N(1)–H(N1)	0.90(2)
H(N1)···O(2)	1.88(2)
N(1)–H(N1)···O(2) (°)	135(2)
C(1)–N(1)–H(N1)	114.5(1.3)
C(5)–O(2)···H(N1)	104.5(7)
(b) within a molecular pair	
N(2)···O(1) (Å)	3.130(2)
N(2)–H(N21)	0.89(2)
H(N21)···O(1)	2.28(2)
N(2)–H(N21)···O(1) (°)	160(2)
C(8)–N(2)–H(N21)	115.9(1.4)
C(3)–O(1)···H(N21)	131.0(6)
(c) between pairs	
N(2)···O(2) (Å)	3.056(2)
N(2)–H(N22)	0.91(3)
H(N22)···O(2)	2.16(3)
N(2)–H(N22)···O(2) (°)	167(2)
C(8)–N(2)–H(N22)	115.1(1.4)
C(5)–O(2)···H(N22)	120.8(6)

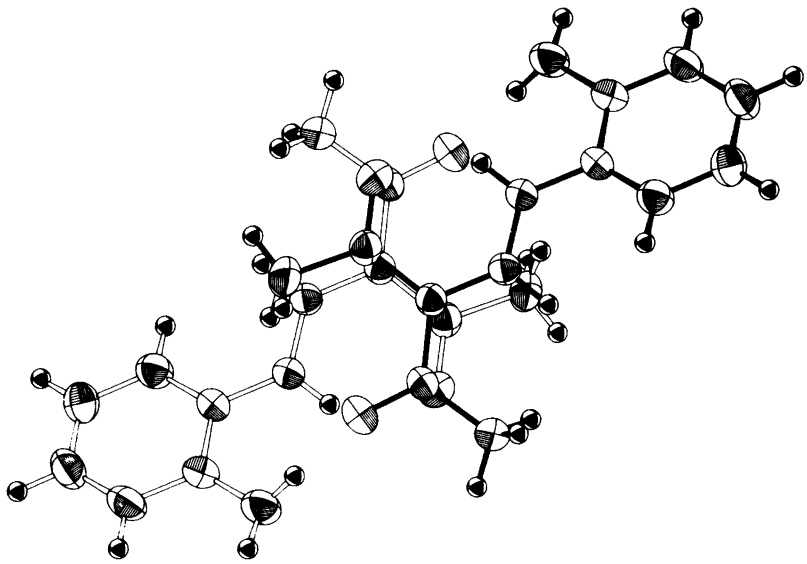

Fig. 2. Overlap diagram of the molecular complex.

while it is normally the angle opposite to the C–O double bond that is less than 120°. The two methyl groups have the same conformation with one of the CH bonds eclipsed with the adjacent carbonyl group.

Intramolecular hydrogen bond. The asymmetric intramolecular hydrogen bond N(1)–H···O has an N···O distance of 2.593(2) Å with the geometry shown in Table 3. The slight rotation of the acetyl oxygen out of the plane of the other atoms in the chelate ring is probably necessary to avoid excessive repulsion. This is a very short hydrogen bond for a neutral molecule, comparable to *e.g.* those in nitromalonamide[15] of 2.580(3) and 2.589(5) Å.

Molecular complex. In the crystal the molecules are arranged in pairs around inversion centres. The approximately planar non-aromatic parts of the molecules overlap as shown in Fig. 2. with an interplanar spacing of 3.45 Å, and the shortest contact, C(3)···O(2), is 3.296(2) Å. Double bonds are arranged alternatingly in the two planes making π-π* electron transfer feasible. This self-complex is further stabilized by two weak hydrogen bonds N–H···O of 3.130(2) Å involving the amino groups and the

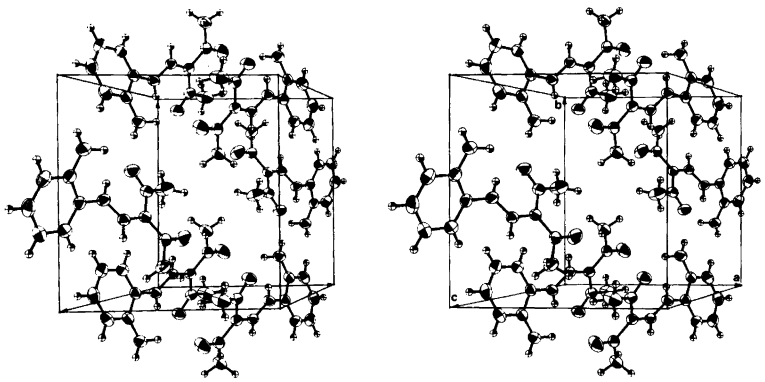

Fig. 3. Stereoscopic view of the molecular packing perpendicular to the *ab*-plane, and with the unit cell outlined.

O(1) atoms. The interplanar spacing is rather long considering the small relative translations in the overlap diagram so the charge transfer interaction is small. The yellow, though intense, colour is another indication of this.

Packing of molecular pairs. The dimeric complexes are arranged in layers, one unit cell thick, parallel to the *bc*-plane. Each pair is connected to the four surrounding units (see Fig. 3) by four hydrogen bonds amino group – carbonyl oxygen O(2) (see Table 3). Thus O(2) accepts one intramolecular and one intermolecular hydrogen bond. Most of the short nonbonded interactions are also within the layer. The weak intermolecular forces in the *a* direction are consistent with the observed crystal morphology.

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