Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

The azo–enaminone 4-(*E*)-amino-3-[(*E*)-2-chlorophenyldiazenyl]pent-3-en-2-one

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.060
wR factor = 0.185
Data-to-parameter ratio = 13.3

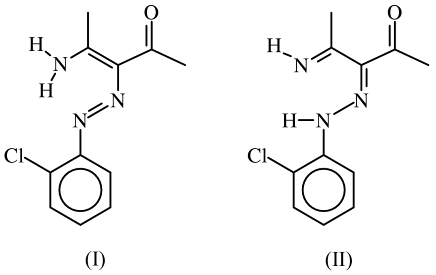
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 26 July 2004
Accepted 12 August 2004
Online 11 September 2004

The title compound, $C_{11}H_{12}ClN_3O$, is composed of a planar azoenamine skeleton, which forms a six-membered ring through an intramolecular hydrogen bond. In the solid state only the azoenamine tautomer was observed. The molecular packing is through adjacent molecules linked by N—H···O bonds, resulting in a two-dimensional sheet structure.

Comment

Although a number of X-ray structural investigations involving simple enaminones have been reported (Cunha *et al.*, 2003; Cunha *et al.*, 2002; Gilli *et al.*, 2000; Kubicki *et al.*, 2000; Dannhardt *et al.*, 1998; Bertolasi *et al.*, 1998), structural analyses of azo-enaminones are relatively scarce (Simunek *et al.*, 2002, Rodrigues *et al.*, 1996; Kettmann *et al.*, 2001). Studies of the molecular packing of enaminones in the solid state are of particular interest because azo-enaminones are compounds with potential non-linear optical properties (Figueiredo & Kascheres, 1997; Oliveira *et al.*, 2003). In addition, azo-enaminones can exist in hydrazoimino/azoenamine tautomeric forms in both solution and the solid state (Kettmann *et al.*, 2001; Simunek *et al.*, 2002). Thus, we prepared the azo-enaminone 4-(*E*)-amino-3-[(*E*)-2-chlorophenylazo]-3-penten-2-one, (I), and undertook its structural analysis. An *ORTEP* (Farrugia, 1997) plot of the molecule and the atomic numbering is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The compound contains an NH_2 hydrogen-bond-donor group, with a Cl atom attached to the aromatic ring.



(I) (II)

With regard to the tautomeric equilibrium, (I) exists predominantly in the azoenamine form in the solid state, as can be seen from the bond lengths along C6—N3—N2—C3—C4—N1 (see Table 1), which are in agreement with others previously reported for azo-enaminones containing an NH_2 group (Rodrigues *et al.*, 1996; Kettmann *et al.*, 2001; Simunek *et al.*, 2002).

According to NMR spectroscopy, no evidence was found for the existence of tautomer (II) in the solution state.

DOI: 10.1107/S1600536804020124

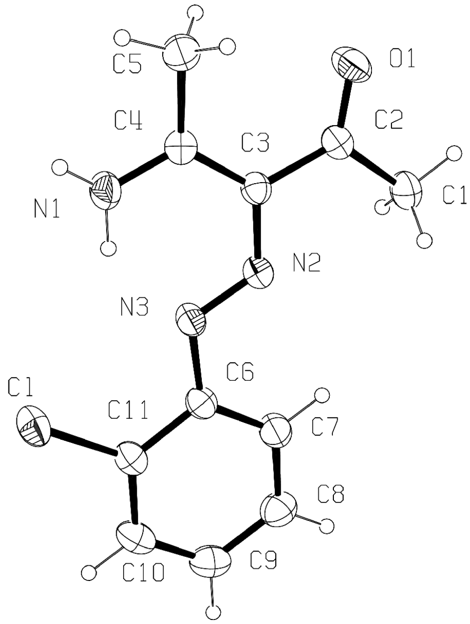


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

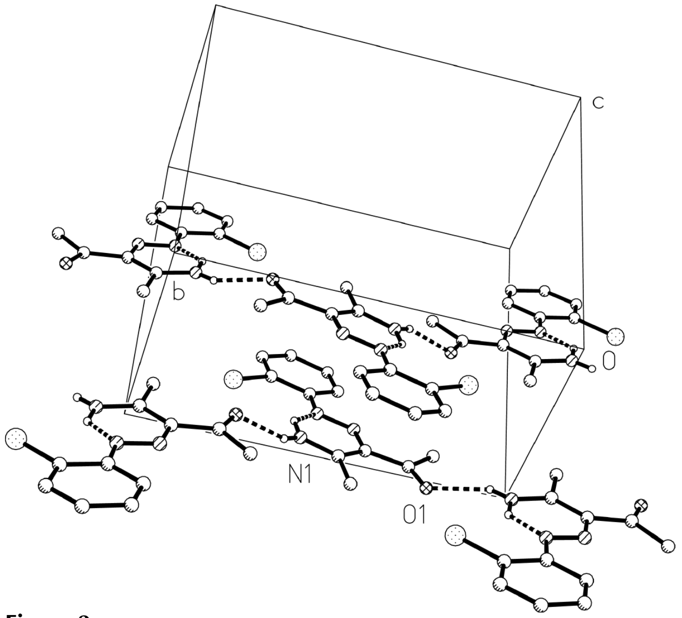


Figure 2
Molecular packing of (I). Intermolecular N—H···O and intramolecular N—H···N hydrogen bonds are shown as dashed lines. Only the H atoms involved in hydrogen bonds are shown for clarity.

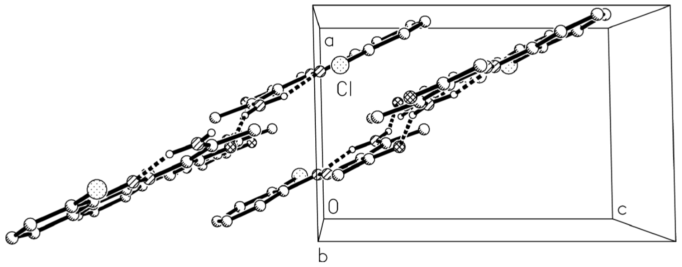


Figure 3
Packing diagram, viewed down the *b* axis, showing the two-dimensional sheet structure formed by the hydrogen bonding network (dashed lines).

However, in the structure determination, the distances N3—N2 = 1.276 (3), N2—C3 = 1.370 (3), C3—C4 = 1.423 (3) and C4—N1 = 1.306 (3) Å are closest to the single and double bonds C—N, N═N and C═C, respectively, in agreement with structural analyses described for analogous azo-enaminones (Kettmann *et al.*, 2001. These small differences made us suspect the presence of a small amount of the tautomer (II) in the structure. However, unequivocal evidence for tautomer (II) was not found in a search for either occupational and orientational/occupational disorder, as reflected by peaks at distances about 0.5 Å from the atoms, while attempts to refine a weak peak located near atom N3 in the difference map as a disordered H-atom site did not improve the model significantly.

Atom H2 on N1 is involved in a strong intramolecular [2.559 (3) Å] hydrogen bond directed towards N3 of the azo group (Table 2). Atom N1 is −0.099 (4) Å from the least-squares plane through atoms C6, N3, N2, C3 and C4. Intramolecular hydrogen bonds therefore contribute to the planarity of this conjugated moiety of (I). In addition, the aromatic ring is coplanar with the enaminone moiety, as indicated by the C7—C6—N3—N2 torsion angle of −0.3 (3)°. The molecular packing of (I) occurs through a hydrogen-bonded network (Figs. 2 and 3, Table 2). In this network, two-dimensional head-to-head molecular-orientated chains are observed, which involve only the enaminone moiety (the head) and not the aromatic ring (the tail).

Experimental

Compound (I) was prepared through the reaction of 4-aminopent-3-en-2-one with the diazonium salt of 2-chloroaniline, in a method analogous to that used previously in the synthesis of other azo-enaminones (Simunek *et al.*, 2002; Kettmann *et al.*, 2001; Figueiredo & Kascheres, 1997). To a solution of 1.2830 g (10 mmol) of 2-chloroaniline in 6 ml of 6 N HCl in 10 ml of water was added dropwise a solution of 0.9771 g (14 mmol) of $NaNO_2$ in 15 ml of water under vigorous magnetic stirring and ice-bath cooling. 26.2 mg of urea was added and the solution was neutralized by the addition of solid Na_2CO_3. 15 ml of CH_2Cl_2 was added, followed by 0.9960 g (10 mmol) of 4-aminopent-3-en-2-one in 20 ml of CH_2Cl_2. The resulting solid was collected by filtration and recrystallized from ethanol, giving 0.9324 g (39% yield) of 4-(*E*)-amino-3-[(*E*)-2-chlorophenylazo]-3-penten-2-one as yellow crystals, m.p. 462–464 K. IR (KBr): 3459, 3224, 1634, 1570, 1442, 1363 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 Hz): δ 2.58 (3H, *s*); 2.60 (3H, *s*); 7.18 (1H, *t*, J = 8.1 Hz); 7.32 (1H, *t*, J = 6.6 Hz); 7.60 (1H, *d*, J = 6.6 Hz); 7.79 (1H, *d*, J = 8.1 Hz); 14.0 (1H, broad).

Crystal data

$C_{11}H_{12}ClN_3O$
M_r = 237.69
Monoclinic, $P2_1/c$
a = 7.673 (6) Å
b = 12.887 (1) Å
c = 11.598 (1) Å
β = 91.28 (2)°
V = 1146.5 (9) Å^3
Z = 4

D_x = 1.377 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11.6–30.0°
μ = 2.81 mm^{-1}
T = 293 (2) K
Irregular, pale yellow
0.35 × 0.13 × 0.12 mm

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan
North *et al.* (1968)
$T_{\min} = 0.649$, $T_{\max} = 0.714$
2335 measured reflections
2038 independent reflections
1756 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.058$
$\theta_{\max} = 67.0°$
$h = -9 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = -1 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: <1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.185$
$S = 1.06$
2038 reflections
153 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1286P)^2 + 0.3565P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.49$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.033 (3)

Table 1
Selected geometric parameters (Å, °).

Cl—C11	1.737 (3)	N2—C3	1.370 (3)
N1—C4	1.306 (3)	N3—C6	1.416 (3)
N2—N3	1.276 (3)	C3—C4	1.423 (3)
C4—N1—H1	121 (2)	N3—N2—C3	118.7 (2)
C4—N1—H2	114.4 (19)	N2—N3—C6	113.78 (19)
H1—N1—H2	124 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H2$\cdots$N3	0.94 (3)	1.79 (3)	2.559 (3)	137 (3)
N1—H1$\cdots$O1$^{\rm i}$	0.82 (3)	2.10 (3)	2.862 (3)	155 (3)

Symmetry code: (i) $1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$.

All phenyl H atoms were placed in calculated positions using a riding model [C—H = 0.93 Å, $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for Csp^2]; the H atoms on N1 were found in the difference Fourier map and refined with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$. The H atoms of the C$sp^3$ atoms C1 and C5 = were placed in calculated positions (C—H = 0.96 Å) and refined as riding, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1993); cell refinement: *CAD*-4/*PC*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

The authors thank the Brazilian Agencies for fellowships to VR (CAPES) and IV (CNPq).

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