Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4-(4-Methoxyphenylamino)-3-phenylazo-3-penten-2-one

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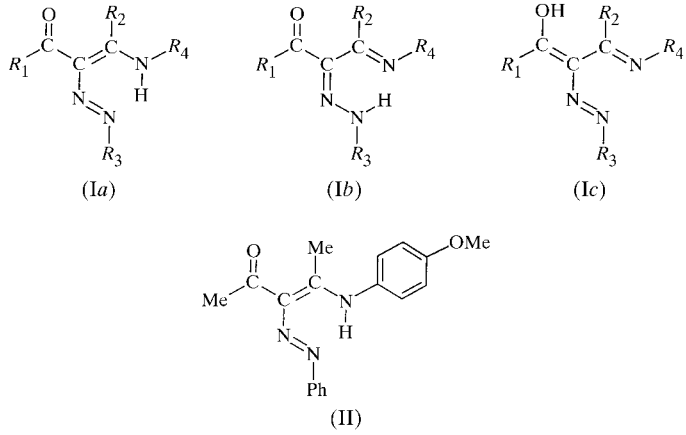
Received 31 January 2001
Accepted 19 March 2001

The title compound, $C_{18}H_{19}N_3O_2$, was obtained by an azo-coupling reaction with enaminones and is composed of a planar azoenamine skeleton which forms a six-membered ring through a symmetrical intramolecular hydrogen bond. The compound was found to exist as an equilibrium mixture of major hydrazoimino and minor azoenamine tautomers. Quantification of the relative contribution of the tautomeric forms is obscured by the existence of the hydrogen bond. Comparison of the results with those obtained for a similar structure revealed a substantial effect on the tautomeric equilibria of the nature of the substituent bonded to the amine nitrogen.

Comment

N-Substituted aminoethylene derivatives having carbonyl function(s) in the β-position – known as enaminones – have been extensively investigated because of their interesting structural characteristics, such as distinct geometric forms and tautomerism (Eberlin *et al.*, 1990). They can also be viewed as push–pull ethylenes, a class of reactive and versatile compounds presenting an unusually low rotational barrier around the C=C double bond with an absorption in the near-ultraviolet and visible regions due to the delocalization of π electrons (Wennerbeck, 1973). Therefore, such compounds have found widespread applications in pharmaceutical and medicinal chemistry, *e.g.* as prodrugs of primary amines or intermediates in the preparation of antiulcer and antibacterial drugs (Naringrekar & Stella, 1990; Vishnu, 1980), as well as in the chemical industry (organic dyes and agrochemicals). The structural and hence the physicochemical variability of enaminones is even increased upon introduction of an azo group to the β-position of the ethylenic bond; such azo-coupling products from enaminones and diazonium ions may, in principle, exist in tautomeric forms (I*a*–*c*). Previous studies have shown that the proportion of individual tautomers depends sensitively on the nature of substituents R_1–R_4; recent results from ^{13}C and ^{15}N NMR spectroscopy have revealed that the title derivative [(II); R_1 = R_2 = Me, R_3 = Ph, R_4 = 4-methoxyphenyl] exists in $CDCl_3$ solution predominantly in the hydrazo form, (I*b*), with a small amount of the azo form, (I*a*) (Macháček *et al.*, 2001). To confirm the NMR results and, at the same time, to establish the structural details, a single-crystal X-ray analysis of (II) was undertaken.



The molecular structure together with the atom-numbering scheme is shown in Fig. 1. As can be seen, the azoenamine grouping (atoms N7, N8, C9, C13 and N15) in the central part of the molecule adopts a planar [r.m.s. deviation 0.014 (2) Å] chelate-like form and is completed to a six-membered ring through an intramolecular hydrogen bond between atoms N7 and N15. The hydrogen bond is symmetrical: the H15 atom

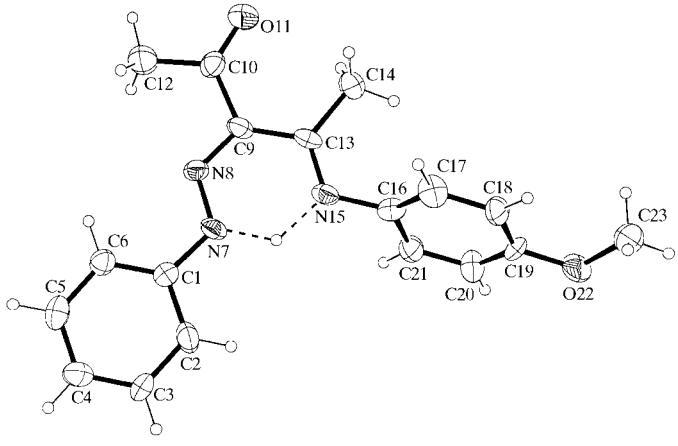


Figure 1
A view of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 35% probability level and H atoms are drawn as small circles of arbitrary radii. Dashed lines indicate the symmetrical intramolecular hydrogen bond.

was found in the difference Fourier synthesis midway between N7 and N15, and was freely refined. The details of this hydrogen bond are: N7···H15 1.35 (3), N15···H15 1.45 (3), N7···N15 2.479 (3) Å and N7···H15···N15 125 (2)°. Of the substituents, the acetyl group and the phenyl ring at N7 are approximately coplanar with the plane of the central six-membered ring, the dihedral angles being 3.5 (2) and 7.3 (2)°, respectively. By contrast, the 4-methoxyphenyl group bonded to the aminic nitrogen (N15) is rotated by 67.7 (1)° from the central molecular plane. Thus, the planarity of the molecule as a whole is perturbed by the 4-methoxyphenyl group.

As noted above, the main purpose of the present work was to identify the tautomer in which the title compound, (II), exists in the solid state [or the percentage of the possible forms (I*a*–*c*) if it exists as an equilibrium mixture]. This can be performed crystallographically by determining the bond orders from the bond-length–bond-order curves proposed by Burke-Laing & Laing (1976). The C9—C13 and C13—N15 bond lengths of 1.473 (4) and 1.271 (3) Å (Table 1), respectively, are close to the values reported for a pure Csp^2—Csp^2 single bond [1.487 (5) Å; Shmueli *et al.*, 1973] and a pure C=N double bond (1.27 Å; Burke-Laing & Laing, 1976). These results are consistent with those obtained from NMR spectroscopy (Macháček *et al.*, 2001), which have indicated that (II) exists in $CDCl_3$ solution as a 90:10 mixture of (I*b*):(I*a*) [with no contribution of (I*c*)]. On the other hand, the N7—N8 and N8—C9 bond distances [1.316 (3) and 1.309 (3) Å, respectively] are both intermediate between single and double bonds (bond orders *ca* 1.4 and 1.7), assuming values of 1.41, 1.23, 1.45 and 1.27 Å for N—N, N=N, C—N and C=N bonds, respectively (Burke-Laing & Laing, 1976). Obviously, if only forms (I*a*) and (I*b*) contribute to the electronic structure of the molecule, then there is a discrepancy in the indications concerning the position of the imine-enamine and azohydrazone tautomerisms. The discrepancy does not seem to be caused by some contribution of the enol form, (I*c*), as indicated by a pure single-bond and a pure double-bond character of the C9—C10 and C10—O11 bonds, respectively (Table 1). Instead, the inconsistency most likely originates from the existence of the symmetrical hydrogen bond [*i.e.* the H atom is not bonded to N7 as required by formula (I*b*)] which should promote an accumulation of electron density on N7 and subsequently its transfer to the adjacent phenyl ring. Indeed, some degree of conjugation of the hydrazone moiety (atoms N7, N8 and C9) with the phenyl ring (which should result in the lowering and increasing of the C9—N8 and N8—N7 bond orders, respectively) is clearly seen in (i) the coplanarity of the hydrazone group with the phenyl ring, (ii) a partial double-bond character of C1—N7, and (iii) a non-equivalency of the phenyl-ring C—C bonds (Table 1).

Another purpose of this work was to compare the present results with those of similar structures in order to explore the effects of substituents R_1–R_4 bonded to the azoenamine skeleton on the position of the tautomeric equilibria in the solid state. However, a search of the Cambridge Structural Database (Allen & Kennard, 1993) for structures containing the azoenamine substructure revealed only one compound, ethyl 2-[(*E*)-5-chloro-2-hydroxy-4-nitrophenylazo]-3-(*E*)-amino-2-butenoate [(III); Rodrigues *et al.*, 1996]. The two compounds, (II) and (III), differ mainly in that (III) contains a primary amine (R_4 = H) instead of the 4-methoxyphenylamine group. The principal characteristics of the two structures are the same with the exception that in (III), the H atom remains bonded to the amine nitrogen, *i.e.* the compound exists predominantly as the azoenamine tautomer, (I*a*). Thus, based on the results obtained from (II) and (III), it may be concluded that the position of the tautomeric equilibria is a sensitive function of the substituents bonded to the terminal azo and amine N atoms (R_3 and R_4).

As the only hydrogen-bond donor of the molecule is involved in the intramolecular hydrogen bond, the intermolecular packing is governed by van der Waals interactions.

Experimental

Compound (II) was prepared by the following procedure: aniline (0.93 g, 10 mmol) in tetrafluoroboric acid (10 ml of *ca* 30% HBF_4) was diazotized by adding a solution of sodium nitrite (0.69 g, 10 mmol) in water (5 ml). After several minutes, sodium tetrafluoroborate (1 g, 9 mmol) was added, the suspension of benzenediazonium tetrafluoroborate formed was mixed, and the precipitated solid collected by suction and thoroughly pressed on a small sintered-glass filter. The almost dry product was added portion-wise to a solution of 4-(4-methoxyphenylamino)-3-penten-2-one (2.26 g, 11 mmol) in diisopropyl ether (15 ml). The mixture was stirred at 273 K for 2 h, whereupon the solid was collected by suction, resuspended in a chloroform–ethyl acetate mixture (1:1, *ca* 10 ml) and transferred onto a silica-gel column. The product was eluted by the same solvent mixture. The fraction containing the product along with the unreacted enaminone was subjected to vacuum distillation to remove the solvent, and the residue was repeatedly triturated with hexane. The less hexane-soluble residue was again submitted to chromatography on a silica-gel column with a chloroform–ethyl acetate mixture (1:1). Finally, the product was recrystallized from cyclohexane (m.p. 411–413 K).

Crystal data

$C_{18}H_{19}N_3O_2$
M_r = 309.36
Monoclinic, $P2_1/c$
a = 11.525 (5) Å
b = 14.465 (6) Å
c = 9.761 (3) Å
β = 92.82 (4)°
V = 1625.3 (11) Å^3
Z = 4
D_x = 1.264 Mg m^{-3}
D_m = 1.27 (1) Mg m^{-3}
D_m measured by flotation in bromoform/cyclohexane
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
θ = 7–18°
μ = 0.08 mm^{-1}
T = 293 (2) K
Plate, yellow
0.30 × 0.25 × 0.10 mm

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
3054 measured reflections
2890 independent reflections
1319 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25.1°
$h = -13 \rightarrow 0$
$k = 0 \rightarrow 17$
$l = -11 \rightarrow 11$
2 standard reflections every 98 reflections
intensity decay: 4%

Refinement

Refinement on F^2
$R(F) = 0.070$
$wR(F^2) = 0.139$
$S = 0.93$
2890 reflections
215 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.11$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C6	1.362 (4)	N7—N8	1.316 (3)
C1—N7	1.394 (3)	N8—C9	1.309 (3)
C1—C2	1.403 (4)	C9—C13	1.473 (4)
C2—C3	1.392 (4)	C9—C10	1.493 (4)
C3—C4	1.372 (4)	C10—O11	1.204 (3)
C4—C5	1.362 (4)	C13—N15	1.271 (3)
C5—C6	1.412 (4)	N15—C16	1.433 (3)
C6—C1—N7	124.2 (3)	C13—C9—C10	123.4 (3)
C6—C1—C2	119.9 (3)	O11—C10—C9	123.0 (3)
N7—C1—C2	115.9 (3)	N15—C13—C9	116.9 (2)
N8—N7—C1	118.3 (2)	N15—C13—C14	124.0 (3)
C9—N8—N7	117.8 (2)	C9—C13—C14	119.1 (3)
N8—C9—C13	125.4 (3)	C13—N15—C16	120.5 (2)
N8—C9—C10	110.9 (3)		
C6—C1—N7—N8	−3.4 (4)	N8—C9—C13—C14	179.5 (3)
C1—N7—N8—C9	178.5 (3)	C10—C9—C13—C14	−6.2 (4)
N7—N8—C9—C13	−3.9 (4)	C9—C13—N15—C16	178.6 (2)
N7—N8—C9—C10	−178.8 (2)	C13—N15—C16—C17	72.1 (4)
N8—C9—C13—N15	1.1 (4)	C20—C19—O22—C23	164.9 (3)

H atoms were treated as riding, with U_{iso} set to 1.2 (1.5 for the methyl H atoms) times U_{eq} of the parent atom, except for the H atom H15 (linking N15 and N7), which was fully refined with respect to positional and U_{iso} parameters.

Data collection: *Syntex* $P2_1$ *Diffractometer Software* (Syntex, 1973); cell refinement: *Syntex* $P2_1$ *Diffractometer Software*; data reduction: *XP*21 (Pavelčík, 1987); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

This work was financially supported by the Grant Agency of the Slovak Republic (project No. 1/8216/01).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1141). Services for accessing these data are described at the back of the journal.

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