

2-Anilinomethylene-3-oxobutane-nitrile: an X-ray and density functional theory study

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Molecules of the title compound, C₁₁H₁₀N₂O, are effectively planar. In the crystal structure, they are stabilized primarily by electrostatic interactions, as the dipole moment of the molecule is 4.56 D. In addition, the molecules are linked by weak C—H···N and C—H···O hydrogen bonds. An analysis of bonding conditions in the molecule was carried out using natural bond orbital (NBO) formalism.

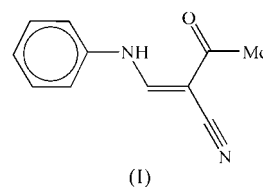
Comment

Push–pull olefins are interesting compounds, not only from a theoretical point of view but also for their interesting spectroscopic properties and numerous applications in organic synthesis (Hermecz *et al.*, 1992; Patai, 1994; Milata & Ilavský, 1995). The structures of some of these compounds have been reported previously, *e.g.* by Lokaj *et al.* (1994) or Kettmann *et al.* (2000, 2004).

Aminomethylene derivatives or β,β -disubstituted aminomethylenes allow the study of the conformation of the —NH—CH= grouping or of the geometrical isomerism of the CH=C double bond, due to the two non-equivalent substituents at the β -positions. If a β -substituent has at least one carbonyl group (C=O) in the acetyl (COOMe) or (m)ethoxycarbonyl (COOEt) substituent, the —NH—CH= group can also be stabilized by an intramolecular hydrogen bond between the NH H atoms and the O atom.

Some compounds of this type having at least one COOMe or COOEt group can be thermally or catalytically cyclized to form the corresponding 3-substituted-4-quinolones (Milata *et al.*, 2000; Hooper, 2001; Coleman, 2004; Blondeau, 1999). If the starting compound does not bear either a COOMe or a

COOEt group, cyclization can also take place through a cyano or other group. In this way, 4-aminoquinolines, interesting as antimalarial drugs and as an apoptosis agent, can also be prepared (Jantová *et al.*, 2006). The precursors for 4-aminoquinolines are anilinoacrylonitriles, *e.g.* anilinoacrylonitrile derivatives of 3-oxobutanenitrile (cyanoacetone), propanedinitrile (malononitrile) or cyanoacetates. Against this background, we present here the crystal structure of the title compound, (I).



The structure of (I) is illustrated in Fig. 1. The molecules in the crystal structure are stabilized primarily by electrostatic interactions, as the calculated dipole moment of the molecule is 4.56 D. In addition, the molecules are linked by weak C—H···N and C—H···O hydrogen bonds (Table 1). The most prominent role in the hydrogen-bonding system is played by atom O1, which is an acceptor of one intra- and two intermolecular hydrogen bonds. The intramolecular N2—H2···O1 hydrogen bond is, however, too long [2.6998 (18) Å] for a H-atom transfer along it. The molecule is almost planar, the largest deviation from planarity being 0.051 (2) Å for atom N1.

Natural bond orbital (NBO) analysis (Foster & Weinhold, 1980) of the molecular electronic structure reveals that the bond orders are, for the majority of the bonds, very close to the expected values (Fig. 2). The exceptions are the N2—C5 and C5—C2 bonds, the bond orders of which are between a single and a double bond, indicating delocalization of electrons. A detailed analysis of the NBO results shows that the electron donor, a lone pair on atom N2, is connected through the C2=C5 double bond to electron-withdrawing groups, *i.e.* —C=O and —CN groups. As a result, the electrons from the lone pair are delocalized to a formally single N2—C5 bond, lending it a partially double-bond character. Furthermore, π -electrons from the C2=C5 double bond are pulled toward the C2—C3 and C2—C1 bonds, which gain a slightly multiple

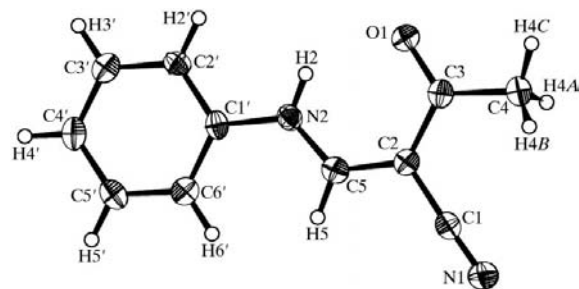


Figure 1

A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

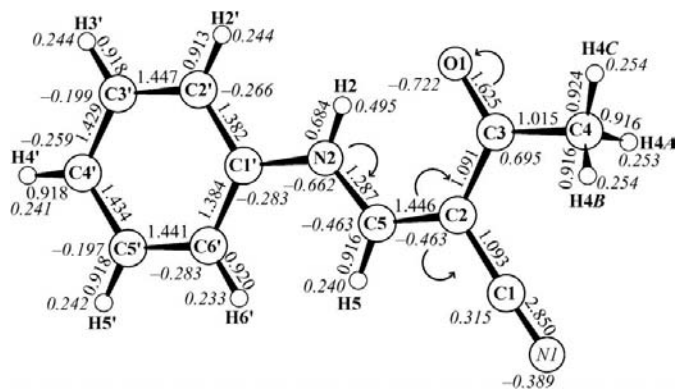


Figure 2

Wiberg bond orders (roman) and natural charges (italics) in $|e|$, calculated for an isolated molecule using NBO formalism. The arrows indicate predicted electron-density transfers.

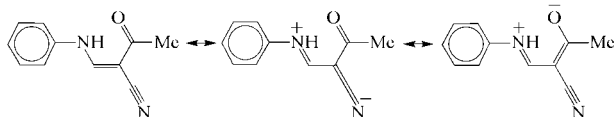


Figure 3

Possible resonance structures of the title compound. Due to the large electron-withdrawing effect of the $-\text{CN}$ group, the structure in the middle is more favoured than the structure on the right.

character (Fig. 3). The expected geometrical consequences of this electron redistribution are a shortening of the $\text{C5}-\text{N2}$ and $\text{C2}-\text{C3}$ bonds, an elongation of the $\text{C2}-\text{C5}$ bond and a planar structure of the moiety attached to the phenyl ring. The planarity of this moiety is further maintained by the intramolecular hydrogen bond $\text{N2}-\text{H2}\cdots\text{O1}$. The geometry of an isolated molecule optimized at the B3LYP/6-31G** level of theory is such that the $\text{C6}'-\text{C1}'-\text{N2}-\text{C5}$ torsion angle is $\sim 13^\circ$, compared with $\sim 1.8^\circ$ found in the crystal. This difference cannot be unambiguously explained by the computational method itself, as the difference in energies between the optimal molecular structure and the planar one (0.1 kJ mol^{-1}) is below the precision of the method.

The orientation of the anisotropic ellipsoid of C1 is unreasonable in its direction, indicating non-statistical uncertainty in the $\text{C1}-\text{N1}$ distance. The length of this bond [$1.146(3) \text{ \AA}$] is in accordance with the value of $1.148(2) \text{ \AA}$ found for a chemically similar push-pull family of compounds surveyed by Ziao *et al.* (2001). It is, however, remarkably longer than two independent $-\text{CN}$ distances ($1.135\text{--}1.136 \text{ \AA}$) reported for anilinomethylenemalononitrile (Nasakin *et al.*, 1992), which differs from (I) by just two $-\text{CN}$ groups attached to the C2 analogue.

Experimental

The title compound can be readily prepared by nucleophilic vinylic substitution of 2-(*m*)ethoxy-3-oxobutanenitrile [2-(*m*)ethoxymethylene cyanoacetone] with aniline, as described by Černuchová *et al.* (2005). Crystals were obtained by recrystallization from toluene.

Crystal data

$\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$
 $M_r = 186.21$
 Monoclinic, $P2_1/n$
 $a = 13.3968(5) \text{ \AA}$
 $b = 5.0656(2) \text{ \AA}$
 $c = 14.3402(5) \text{ \AA}$
 $\beta = 108.027(1)^\circ$
 $V = 925.39(6) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.337 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 173(2) \text{ K}$
 Plate, colourless
 $0.22 \times 0.14 \times 0.02 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.981$, $T_{\max} = 0.998$

11777 measured reflections
 2298 independent reflections
 1514 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 28.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.124$
 $S = 1.01$
 2298 reflections
 138 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.4176P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$); the values in the second of each pair of rows are from the solid-state density functional theory calculations.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}$	0.88	2.04	2.6998 (18)	130.7
$\text{C2}'-\text{H2}'\cdots\text{O1}^{\text{i}}$	1.04	1.81	2.6490	134.6
$\text{C4}-\text{H4A}\cdots\text{O1}^{\text{ii}}$	0.95	2.40	3.302 (3)	159.1
	1.09	2.20	3.2783	167.2
$\text{C5}-\text{H5}\cdots\text{N1}^{\text{iii}}$	0.98	2.57	3.545 (2)	170.9
	1.10	2.40	3.4897	168.9
	0.95	2.43	3.365 (2)	167.2
	1.09	2.25	3.3300	170.3
$\text{C6}'-\text{H6}'\cdots\text{N1}$	0.95	2.69	3.635 (4)	173.5
	1.09	2.46	3.5393	172.6

Symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$;

For the X-ray data, H atoms were refined isotropically and constrained to ideal geometry using an appropriate riding model. The $\text{C}-\text{H}$ distance was kept fixed at 0.98 \AA for tertiary H atoms and at 0.95 \AA for secondary H atoms, and the $\text{N}-\text{H}$ distance was kept fixed at 0.88 \AA .

Molecular calculations were carried out at the B3LYP/6-31G** level of theory using GAUSSIAN98 (Frisch *et al.*, 1998). NBO (natural bond order) calculations were carried out using the NBO program (Glendening *et al.* 1993) included in the GAUSSIAN package.

Theoretical investigation of hydrogen bonds in the crystal was performed using the Vienna *ab initio* simulation package VASP (Kresse & Furthmüller, 1996; Kresse & Hafner, 1993). The calculations were based on density functional theory (DFT) with periodic boundary conditions (Jones & Gunnarsson, 1989) using generalized gradient approximation (GGA) in the exchange-correlation function (Perdew *et al.*, 1992). The interactions between ions and electrons were described using the projector-augmented wave method (PAW) (Kresse & Joubert, 1999), with a plane wave cut-off of 400 eV . The optimization of the structure was carried out by the method of conjugated gradients in four k points (Teter *et al.*, 1989; Bylander *et al.*, 1990).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3022). Services for accessing these data are described at the back of the journal.

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