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Crystal structure of (*Z*)-4-(phenylamino)pent-3-en-2-one, $C_{11}H_{13}NO$, at 200 K

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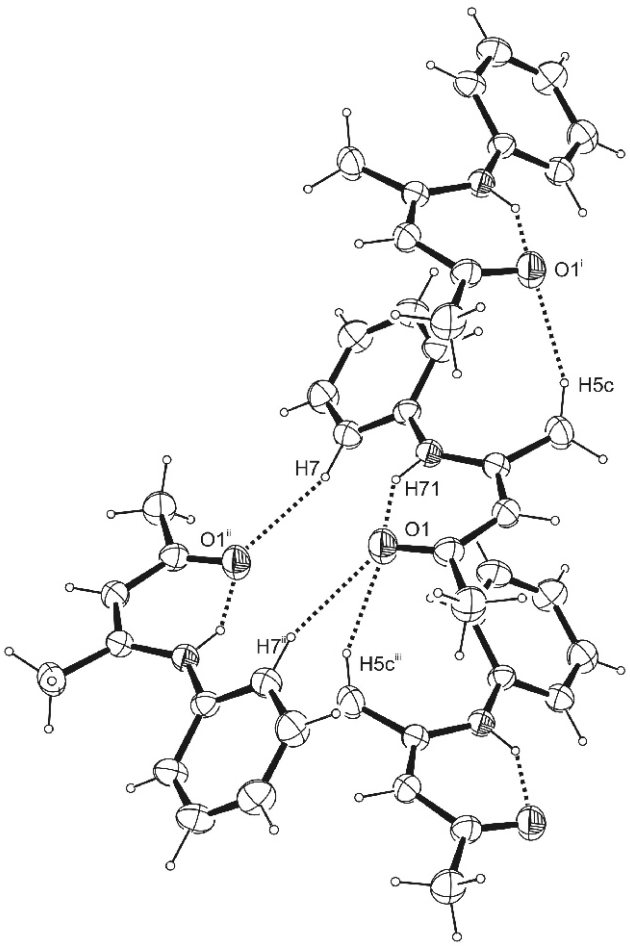

Abstract

$C_{11}H_{13}NO$, monoclinic, $P12_1/c1$ (no. 14), a = 9.0532(3) Å, b = 10.9311(3) Å, c = 10.1107(3) Å, β = 107.171(1)°, V = 956.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.124, T = 200 K.

Source of material

The compound was prepared upon acid-catalyzed condensation of aniline and acetylacetone in toluene under constant azeotropic removal of the reaction water liberated. After removal of the solvent an oil was obtained that slowly crystallized at room temperature yielding big crystals suitable for X-ray analysis.

Experimental details

Carbon-bound H-atoms were placed in calculated positions (d(C—H) = 0.95 Å for aromatic C atoms and the central C atom of the chain) and were included in the refinement in the riding model approximation, with U(H) set to 1.2 U_{eq}(C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density (HFIX 137 option in the SHELX program suite [1]), their U(H) invariably set to 1.5 U_{eq}(C). The nitrogen-bound H atom was located on a difference Fourier map and refined freely.

Discussion

Schiff-base-type bidentate *N*,*O*-ligands have found widespread use in coordination chemistry. In general, they are easily obtained upon acid-catalyzed condensation reaction of a primary amine and a diketone. If a 1,3-diketone such as acetylacetone or dibenzoylmethane is used, tautomery between the imine, the enamine and the enol structure significantly enhances the versatility of the ligand and allows for different modes of chelation of transition metals. At room temperature, the title compound was found to exist in its enamine tautomer [2]. In our continuous efforts to elucidate the principles guiding the formation of coordination compounds based on Schiff-base-type bidentate *N*,*O*-ligands , we determined the crystal structure of the title compound at low temperature to enable comparative studies.

Based on d(C—C) along the OC–C–CN moiety as well as the presence of an electron density close to the nitrogen atom which could unambiguously be assigned to a hydrogen atom, it was concluded that the title compound is present in its enamine form. The molecule is in (*Z*)-configuration. The phenyl ring is not completely in plane with the other atoms of the molecule. The least-squares planes defined by the atoms of the carbocycle as well as the OC–C–CN moiety, respectively, enclose an angle of 31.18(5)°. The presence of the title compound as its (*Z*)-configured enamine tautomer in the solid state might be facilitated by the formation of an intramolecular N–H···O hydrogen bond. In terms of graph-set analysis [3,4], the descriptor for this contact would be $S(6)$. Furthermore, two different types of C–H···O contacts whose range falls slightly below the sum of van-der-Waals radii of the respective atoms are observed in the crystal structure. The first set of these contacts is supported by one of the H atoms of the phenyl group in *ortho*-position to the N atom and connects two molecules to centrosymmetric dimers. The second type of C–H···O contacts stems from one of the H atoms of the methyl group closest to the nitrogen atom. The descriptor for the first set of contacts on the unitary level is $R_2^2(8)$ while the descriptor for the second set of contacts on the same level is $C_1^1(6)$. In total, the carbonylic O atom serves as threefold acceptor, and the molecules

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are connected to layers perpendicular to the crystallographic *a* axis with the phenyl groups forming a hydrophobic outside layer on both sides. The π stacking is not a dominant feature in the crystal structure with the closest Cg···Cg distance measured at 5.7854(7) Å.

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.296 × 0.493 × 0.504 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.78 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	56.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17019, 2369
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2131
$N(param)_{refined}$:	124
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-3 [5], Mercury [6], PLATON [7]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(71)	4*e*	0.958(2)	0.648(2)	0.127(2)	0.050(4)
H(1A)	4*e*	1.3865	0.7156	0.0395	0.063
H(1B)	4*e*	1.3245	0.8532	0.0126	0.063
H(1C)	4*e*	1.2660	0.7521	–0.1058	0.063
H(3)	4*e*	1.1299	0.9137	0.0971	0.037
H(5A)	4*e*	0.7846	0.9206	0.1666	0.058
H(5B)	4*e*	0.9275	1.0022	0.1562	0.058
H(5C)	4*e*	0.9331	0.9361	0.2988	0.058
H(7)	4*e*	0.7348	0.5249	0.0736	0.039
H(8)	4*e*	0.5310	0.4488	0.1461	0.047
H(9)	4*e*	0.4584	0.5461	0.3231	0.049
H(10)	4*e*	0.5965	0.7165	0.4322	0.047
H(11)	4*e*	0.8044	0.7914	0.3647	0.041

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	1.1231(1)	0.62656(7)	0.04880(9)	0.0481(5)	0.0299(4)	0.0561(5)	–0.0009(3)	0.0324(4)	–0.0017(3)
N(1)	4*e*	0.9130(1)	0.70551(8)	0.16374(9)	0.0327(4)	0.0262(4)	0.0326(4)	0.0021(3)	0.0174(3)	0.0000(3)
C(1)	4*e*	1.2970(1)	0.7668(1)	–0.0057(1)	0.0395(6)	0.0419(6)	0.0525(7)	–0.0012(5)	0.0273(5)	0.0021(5)
C(2)	4*e*	1.1643(1)	0.7354(1)	0.0504(1)	0.0321(5)	0.0341(5)	0.0328(5)	0.0001(4)	0.0153(4)	0.0017(4)
C(3)	4*e*	1.0915(1)	0.83324(9)	0.1007(1)	0.0345(5)	0.0281(5)	0.0331(5)	–0.0027(4)	0.0139(4)	–0.0005(4)
C(4)	4*e*	0.9692(1)	0.81876(9)	0.1543(1)	0.0317(5)	0.0280(5)	0.0258(4)	0.0017(4)	0.0093(4)	–0.0007(3)
C(5)	4*e*	0.8974(1)	0.9289(1)	0.1977(1)	0.0461(6)	0.0284(5)	0.0467(6)	0.0030(4)	0.0226(5)	–0.0034(4)
C(6)	4*e*	0.7875(1)	0.66754(9)	0.20948(9)	0.0267(4)	0.0295(5)	0.0261(4)	0.0039(3)	0.0105(3)	0.0032(3)
C(7)	4*e*	0.7067(1)	0.5644(1)	0.1464(1)	0.0351(5)	0.0322(5)	0.0338(5)	0.0011(4)	0.0145(4)	–0.0017(4)
C(8)	4*e*	0.5854(1)	0.5193(1)	0.1894(1)	0.0356(6)	0.0381(6)	0.0457(6)	–0.0057(4)	0.0148(5)	–0.0031(5)
C(9)	4*e*	0.5429(1)	0.5763(1)	0.2951(1)	0.0311(5)	0.0488(7)	0.0470(6)	–0.0016(4)	0.0196(5)	0.0030(5)
C(10)	4*e*	0.6247(1)	0.6775(1)	0.3593(1)	0.0385(6)	0.0489(7)	0.0370(5)	0.0012(5)	0.0213(5)	–0.0032(5)
C(11)	4*e*	0.7476(1)	0.7228(1)	0.3185(1)	0.0355(5)	0.0404(6)	0.0290(5)	–0.0033(4)	0.0141(4)	–0.0047(4)

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