Eric C. Hosten and Richard Betz*

Crystal structure of *N*-benzyl-*N*-nicotinoyl-nicotine amide $C_{19}H_{15}N_3O_2$

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	$0.42 \times 0.31 \times 0.09$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$	14,466, 3845, 0.060
$N(hkl)_{\text{unique}}$, R_{int} :	
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2495
$N(\text{param})_{\text{refined}}$:	217
Programs:	Bruker [1, 6], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

<https://doi.org/10.1515/ncrs-2020-0428>

Received August 3, 2020; accepted September 15, 2020;

published online October 5, 2020

Abstract

$C_{19}H_{15}N_3O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 18.4336(13)$ Å, $b = 6.0321(4)$ Å, $c = 15.0585(10)$ Å, $\beta = 112.171(3)^\circ$, $V = 1550.60(18)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0535$, $wR_{\text{ref}}(F^2) = 0.1298$, $T = 200$ K.

CCDC no.: 2032084

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the diffraction studies were taken directly from the provided product.

*Corresponding author: Richard Betz, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa, E-mail: Richard.Betz@mandela.ac.za. <https://orcid.org/0000-0002-5730-2152>

Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth, 6031, South Africa. <https://orcid.org/0000-0003-4173-2550>

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for methylene groups) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2 U_{\text{eq}}(C)$.

Comment

Chelate ligands have found widespread use in coordination chemistry due to the increased stability of coordination compounds they can form in comparison to monodentate ligands. The stability of these compounds is enhanced further if the denticity of the ligand is increased upon incorporation of more potential donor sites [7]. While cyclic systems (such as crown ethers, cryptands, sarcophagins and seculchates) additionally benefit from the macrocyclic effect and give rise to the formation of some of the most stable coordination compounds known to mankind, a different picture is at hand for open-chain type ligands where, also factors such as pH values in case of deprotonable functional groups come into play. This is for instance the case for EDTA, whose importance in complexometric titrations is well established already in fundamental laboratory courses for undergraduate students. Much less data are at hand for ligands that derive their multidenticity strictly

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
O1	0.24463 (8)	1.0117 (2)	0.25493 (11)	0.0352 (4)
O2	0.13325 (8)	0.3873 (2)	0.09366 (10)	0.0362 (4)
N1	0.18767 (9)	0.6996 (2)	0.17529 (11)	0.0233 (3)
N11	0.41661 (10)	0.4164 (3)	0.34356 (13)	0.0360 (4)
N21	0.32975 (10)	0.2468 (3)	0.03141 (13)	0.0364 (4)
C1	0.25322 (11)	0.8250 (3)	0.23072 (13)	0.0235 (4)
C2	0.18701 (11)	0.5190 (3)	0.11679 (13)	0.0251 (4)
C3	0.11225 (11)	0.7653 (3)	0.18148 (13)	0.0266 (4)
H3A	0.0687	0.7038	0.1256	0.032*
H3B	0.1078	0.9289	0.1782	0.032*
C11	0.33222 (10)	0.7216 (3)	0.26705 (12)	0.0228 (4)
C12	0.34514 (11)	0.5044 (3)	0.30049 (13)	0.0271 (4)
H12	0.3009	0.4137	0.2923	0.033*
C13	0.47766 (13)	0.5474 (4)	0.35436 (16)	0.0388 (5)
H13	0.5288	0.4880	0.3850	0.047*
C14	0.47049 (12)	0.7649 (4)	0.32333 (16)	0.0401 (5)
H14	0.5157	0.8511	0.3316	0.048*
C15	0.39692 (12)	0.8545 (3)	0.28042 (14)	0.0328 (5)
H15	0.3905	1.0049	0.2602	0.039*
C21	0.24958 (10)	0.5000 (3)	0.07764 (12)	0.0231 (4)
C22	0.27853 (11)	0.2916 (3)	0.07211 (13)	0.0279 (4)
H22	0.2607	0.1715	0.0993	0.033*
C23	0.35307 (12)	0.4180 (4)	−0.00727 (14)	0.0349 (5)
H23	0.3887	0.3905	−0.0380	0.042*
C24	0.32828 (13)	0.6322 (4)	−0.00497 (14)	0.0346 (5)
H24	0.3474	0.7490	−0.0325	0.042*
C25	0.27545 (12)	0.6759 (3)	0.03773 (13)	0.0300 (4)
H25	0.2572	0.8224	0.0398	0.036*
C31	0.10417 (10)	0.6858 (3)	0.27246 (12)	0.0223 (4)
C32	0.12922 (11)	0.4761 (3)	0.31025 (14)	0.0276 (4)
H32	0.1549	0.3822	0.2807	0.033*
C33	0.11683 (11)	0.4038 (3)	0.39060 (14)	0.0301 (4)
H33	0.1344	0.2610	0.4163	0.036*
C34	0.07895 (11)	0.5387 (4)	0.43358 (14)	0.0332 (5)
H34	0.0705	0.4885	0.4887	0.040*
C35	0.05347 (12)	0.7461 (4)	0.39642 (14)	0.0339 (5)
H35	0.0270	0.8384	0.4256	0.041*
C36	0.06653 (11)	0.8198 (3)	0.31638 (14)	0.0278 (4)
H36	0.0495	0.9636	0.2915	0.033*

from sigma donor, electrically neutral sites. At the onset of a study aimed at deriving the rules guiding the principles of complexation tendencies for such ligands, the title compound was seen as a tempting starting compound. To allow for the comparison of metrical parameters in the free ligand as well as envisioned coordination compounds of a series of transition metals, rare earth metals, actinides and elements from the main groups, the crystal structure of the free ligand was determined. Similar compounds featuring nitrogen atoms next to keto or thioketo groups have been characterized in the solid state already [8–11].

The title compound is a derivative of nicotinic amide. The nitrogen atom of the amide group features a benzyl group as well as a nicotinoyl moiety instead of its two hydrogen atoms as bonding partners. The C–O bond lengths are almost identical in length with values of 1.213(2) Å and 1.214(2) Å, and do not show signs of pronounced amide-type resonance stabilization as the pertaining elongation of the C=O bonds is only found at the shorter end compared to other tertiary acid amides as found in the Cambridge Structural Database [12]. The least-squares planes defined by the non-hydrogen atoms of the three aromatic moieties enclose angles of 25.61(11)°, 48.64(6)° and 66.94(6)°, with the smallest and the largest angle of intersection found for the two heterocyclic systems towards the phenyl ring.

In the crystal, C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii are present. One such contact is established between the hydrogen atom in *ortho*-position with respect to the intracyclic pnictogen atom N11 and to C11. In terms of graph-set analysis [13, 14], the descriptor for these contacts is C₁¹ (7) at the unary level. An intramolecular C–H···O and a intermolecular C–H···N contact are also present; these can be described as S7 and C11(7), respectively, using graph set notation. In total, the molecules are connected to infinite chains along the crystallographic *b* axis. While π -stacking is not a prominent stabilizing feature of the crystal structure of the title compound, with the shortest distance between two centers of gravity being measured at 4.0191(11) Å, one could discuss the presence of a C–H··· π interaction between one of the hydrogen atoms on the phenyl moiety and its symmetry-generated equivalents; however, the corresponding C–H··· π angle of 131° deviates significantly from linearity.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The corresponding author thanks the National Research Foundation for financial support.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. *APEX2, SAINT and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.
3. Farrugia L. J. *WinGX and ORTEP for Windows*: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.

4. Macrae C. F., Bruno I. J., Chisholm J. A., Edgington P. R., McCabe P., Pidcock E., Rodriguez-Monge L., Taylor R., van de Streek J., Wood P. A. *Mercury CSD 2.0* – new features for the visualization and investigation of crystal structures. *J. Appl. Crystallogr.* 2008, *41*, 466–470.
5. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
6. Bruker. *SADABS*; AXS Inc.: Madison, WI, USA, 2008.
7. Gade L. H. *Koordinationschemie, 1. Auflage*; Wiley-VCH: Weinheim, 1998.
8. Masu H., Ohmori K., Kishikawa K., Yamamoto M., Yamaguchi K., Kohmoto S. Creation of concave-shaped conformation in crystal structures using an iminodicarbonyl linker. An application to solid-state intramolecular [4 + 4] photocycloaddition reactions of 2-pyridone derivatives. *Bull. Chem. Soc. Jpn.* 2005, *78*, 1127–1131.
9. Potgieter K., Hosten E., Gerber T., Betz R. 4-((E)-{2-[N-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-di-hydro-1H-pyrazol-4-yl)carboximido-yl]benzyl-idene}amino)-1,5-di-methyl-2-phenyl-2,3-di-hydro-1H-pyrazol-3-one. *Acta Crystallogr.* 2011, *E67*, o2785–o2786.
10. Betz R., Gerber T. Ammonium 4,6-dioxo-2-sulfanylidene-1,3-diazinan-5-ide. *Acta Crystallogr.* 2011, *E67*, o1326.
11. Betz R., Schalekamp H., Gerber T. Bis(piperidin-1-yl)methanone. *Acta Crystallogr.* 2011, *E67*, 397.
12. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
13. Bernstein J., Davis R. E., Shimon L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1555–1573.
14. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.