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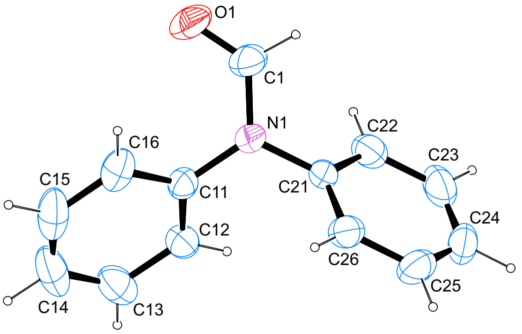
Crystal structure of *N,N*-diphenylformamide, $C_{13}H_{11}NO$



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Abstract

$C_{13}H_{11}NO$, orthorhombic, $Pca2_1$ (no. 29), a = 23.801(4) Å, b = 6.0510(13) Å, c = 7.2677(14) Å, V = 1046.7(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0335, $wR_{ref}(F^2)$ = 0.0896, T = 200 K.

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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 (Hopkin & Williams Ltd). Crystals suitable for the diffraction study were taken directly from the provided material.

Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	0.53 × 0.41 × 0.19 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.0°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8805, 2435, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2215
$N(param)_{refined}$:	136
Programs:	Bruker [1, 2], SHELX [3], WinGX/ ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2 U_{eq}(C).

The refinement resulted in a Flack parameter with an unusually high e.s.d. value. Due to the absence of a strong anomalous scatterer, the item was removed from the CIF in agreement with IUCR recommendations for the pertaining C Level alert.

Comment

Coordination compounds of transition metals find vast application in modern industrial processes. The interplay of coordination numbers, oxidation states as well as the nature of the ligands present in such compounds can give rise to a vast collection of physicochemical properties that can be exploited for catalytic pathways. Especially the variation of ligands – their electronic properties as well as their spatial pretense – can be exploited to fine-tune the inherent reactivity and suitability of coordination compounds for specific synthetic applications. Amides belong to one class of ligands that has received relatively little attention. At the start of a research project aimed at elucidating the potential of simple amides as ligands in coordination compounds, the title compound was chosen as a starting point as it is a derivative of the simplest amide,

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.20491(8)	0.1138(3)	1.1184(2)	0.0623(5)
N1	0.15502(7)	0.2760(3)	0.8851(2)	0.0357(4)
C1	0.20289(9)	0.2146(4)	0.9744(3)	0.0476(5)
H1	0.237636	0.254101	0.919125	0.057*
C11	0.10008(8)	0.2313(3)	0.9566(3)	0.0338(4)
C12	0.05935(8)	0.3943(3)	0.9475(3)	0.0384(4)
H12	0.067806	0.532495	0.891941	0.046*
C13	0.00625(9)	0.3563(4)	1.0193(3)	0.0518(6)
H13	−0.021596	0.468461	1.012349	0.062*
C14	−0.00630(12)	0.1572(5)	1.1003(4)	0.0623(7)
H14	−0.042573	0.132103	1.150692	0.075*
C15	0.03386(13)	−0.0052(5)	1.1080(3)	0.0614(7)
H15	0.024988	−0.143169	1.163281	0.074*
C16	0.08721(10)	0.0287(4)	1.0365(3)	0.0478(5)
H16	0.114631	−0.085169	1.042042	0.057*
C21	0.15990(7)	0.4173(3)	0.7270(3)	0.0323(4)
C22	0.18657(8)	0.6188(4)	0.7428(3)	0.0436(5)
H22	0.201837	0.663403	0.857690	0.052*
C23	0.19106(10)	0.7557(4)	0.5914(4)	0.0579(7)
H23	0.210066	0.893198	0.601713	0.069*
C24	0.16818(11)	0.6936(4)	0.4267(4)	0.0608(7)
H24	0.170760	0.789279	0.323431	0.073*
C25	0.14137(10)	0.4925(5)	0.4101(3)	0.0559(6)
H25	0.125755	0.449763	0.295176	0.067*
C26	0.13713(9)	0.3522(4)	0.5609(3)	0.0413(5)
H26	0.118809	0.213298	0.549843	0.050*

formamide. To allow for comparative studies regarding metrical parameters that coordination might have on the ligands the molecular and crystal structure of the title compound were determined. To the best of our knowledge, only the data of one rhenium complex featuring the title compound as ligand has been reported in the literature twice [7, 8], however, in one case no 3D coordinates were deposited [8] with the Cambridge Structural Database [9]. Furthermore, the crystal structure of *N*-(3-t-butyl-2-hydroxy-5-methoxyphenyl)-*N*-(2-hydroxy-5-methylphenyl)formamide has been reported earlier [10].

The structure solution shows the derivative of formamide bearing two phenyl moieties on the nitrogen atom. The C=O bond length of 1.212(3) Å is not indicative of marked amide-type resonance stabilization while the C–N bond length of 1.365(2) Å towards the formyl group shows some shortening in comparison to common C–N single bonds. A possible explanation for this finding could be ascribed to the presence of the two aromatic systems on the nitrogen atom that might compete for the lone pair on the pnicogen atom. The pertaining C–N bond lengths of 1.433(2) Å and 1.437(2) Å, respectively, are slightly shorter than the most common values reported for $C_{(ar)}$-N bonds in compounds whose metrical parameters have been secured on grounds of diffraction studies based on single crystals. The two phenyl groups are orientated almost perpendicular to one another with the least-squares planes as defined by the respective non-hydrogen atoms of each aromatic moiety intersecting at an angle of 83.68(10)°.

In the crystal, C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the participating atoms can be observed. These are supported by one of the hydrogen atoms in *meta* and the hydrogen atom in *para* position to the nitrogen atom on only one of the two phenyl groups as donors. In terms of graph-set analysis [11, 12], the descriptor for these contacts is $C_1^1(7)C_1^1(8)$ at the unary level. In total, the molecules are connected to double layers perpendicular to the crystallographic *a* axis. π-stacking is not a prominent feature in the crystal structure of the title compound as the shortest intercentroid distance was measured at 4.8632(16) Å, which is observed exclusively between the aromatic system whose hydrogen atoms do not support the C–H···O contacts and its symmetry-generated equivalents.

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