Redetermination of the crystal structure of *N*,*N*-diphenylacetamide, at 200 K, $C_{14}H_{13}NO$

Eric Hosten and Richard Betz*

Nelson Mandela Metropolitan University, Summerstrand Campus, Department of Chemistry, University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa

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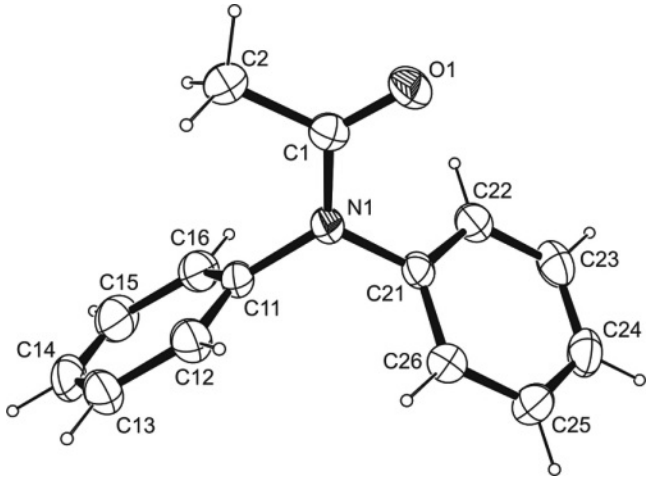

Abstract

$C_{14}H_{13}NO$, orthorhombic, *Pbca* (no. 61), a = 10.9317(3) Å, b = 11.9675(4) Å, c = 17.2285(5) Å, V = 2253.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.0340, $wR_{ref}(F^2)$ = 0.0879, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.319×0.579×0.590 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.79 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	54.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10786, 2581
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2246
$N(param)_{refined}$:	148
Programs:	SHELX [9], ORTEP-3 [10], MERCURY [11], PLATON [12]

Source of material

The title compound was obtained commercially (Aldrich). Crystals suitable for the X-ray diffraction study were taken directly from the provided product.

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_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl group were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 127 in the SHELX program suite [9], with U_{iso}(H) set to 1.5U_{eq}(C). The hydrogen atoms of the methyl group show a disorder over two positions with site occupancy factors of 0.80 and 0.20.

* Correspondence author (e-mail: Richard.Betz@nmmu.ac.za)

Discussion

Chelate ligands have found widespread use in coordination chemistry due to the enhanced thermodynamic stability of resultant compounds in relation to coordination compounds exclusively applying comparable monodentate ligands only [1]. Combining different sets of donor atoms in one chelate ligand molecule, a probe for testing and accomodating metal centers of different Lewis acidities is at hand. The title compound, which features an *N*,*N*-disubstituted amide group, seemed particularly interesting in this aspect as it may act both as a mono- as well as a bidentate ligand generating four-membered chelate rings. Amide-type resonance might enhance the tendency of the title compound to act exclusively as a monodentate ligand while fine tuning of the spatial and electronic properties of the central atom might increase its propensity to act as a bidentate ligand. The molecular and crystal structure of the title compound has been reported earlier by Krigbaum et al., however, at room temperature only [2]. In addition, no discussion of intra- or intermolecular interactions in the crystalline state was conducted by these authors. In continuation of preliminary studies about the structures of various *N*- and *O*-donor atom ligand systems [3–5], the crystal and molecular structure of the title compound was re-determined to allow for comparisons of metrical parameters with envisioned coordination compounds at lower temperatures. The title structure is shown in the figure. The two least-squares planes defined by the respective carbon atoms of the phenyl groups bonded to the nitrogen atom enclose an angle of 69.69(4)°. These latter two planes intersect with the least-squares plane defined by atoms C2–C1–O1–N1–C11–C21 at angles of 60.22(5)° and 84.15(5)°. The O–C–N–C_{ar} dihedral angles are found at –2.69(15)° and 175.39(9)°. This is indicative of a nearly planar arrangement of this moiety and can be attributed to amide-type resonance. The latter finding is in good agreement with metrical values apparent in the literature as a survey among the data deposited with the CSD [6] for *N*,*N*-disubstituted (alkyl or aryl moieties) amides reveals. The occurrence of amide resonance also becomes apparent by the shortening of the C1–N bond length as well as the elongation of the C=O bond length in comparison to isolated C–N single and C=O double bonds. A comparison with the metrical values reported for the molecular structure determined at room temperature [2] reveals – apart from one nitrogen-phenyl bond – the amide-moiety based bond lengths to be invariably shorter at room temperature. 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 are observed. These are exclusively supported by one of the hydrogen atoms in *meta* position to the nitrogen atom. The oxygen atom serves as acceptor. Additionally, a C–H···π interaction is observed. In terms of graph-set analysis [7,8], the C–H···O contacts require a $C^1_1(7)$ descriptor on the

unary level. In total, the molecules are connected to chains along the crystallographic *b* axis.

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(2A)	8*c*	0.2	0.5316	0.1156	0.4662	0.053
H(2B)	8*c*	0.2	0.6520	0.1445	0.4173	0.053
H(2C)	8*c*	0.2	0.5607	0.0491	0.3877	0.053
H(2D)	8*c*	0.8	0.6312	0.0905	0.3813	0.053
H(2E)	8*c*	0.8	0.5108	0.0616	0.4302	0.053
H(2F)	8*c*	0.8	0.6022	0.1571	0.4597	0.053
H(12)	8*c*		0.2601	0.1077	0.4615	0.043
H(13)	8*c*		0.2082	0.0701	0.5910	0.056
H(14)	8*c*		0.2915	0.1760	0.6909	0.062
H(15)	8*c*		0.4259	0.3207	0.6630	0.059
H(16)	8*c*		0.4742	0.3635	0.5342	0.045
H(22)	8*c*		0.4853	0.4499	0.3445	0.038
H(23)	8*c*		0.3755	0.5899	0.2804	0.045
H(24)	8*c*		0.1637	0.5749	0.2674	0.048
H(25)	8*c*		0.0619	0.4194	0.3162	0.047
H(26)	8*c*		0.1709	0.2787	0.3799	0.038

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)	8*c*	0.51665(7)	0.22582(7)	0.29988(4)	0.0402(4)	0.0421(4)	0.0259(4)	0.0057(3)	0.0082(3)	–0.0013(3)
N(1)	8*c*	0.40560(7)	0.26449(7)	0.40713(5)	0.0288(4)	0.0311(4)	0.0210(4)	0.0049(3)	0.0031(3)	0.0037(3)
C(1)	8*c*	0.49544(9)	0.20737(8)	0.36820(6)	0.0263(5)	0.0288(5)	0.0267(5)	–0.0008(4)	0.0015(4)	–0.0019(4)
C(2)	8*c*	0.5661(1)	0.12168(9)	0.41384(7)	0.0333(5)	0.0356(6)	0.0381(6)	0.0080(4)	0.0027(4)	0.0026(4)
C(11)	8*c*	0.37229(9)	0.23914(9)	0.48608(5)	0.0286(5)	0.0328(5)	0.0214(5)	0.0075(4)	0.0022(4)	0.0043(4)
C(12)	8*c*	0.2933(1)	0.15173(9)	0.50231(7)	0.0376(6)	0.0354(6)	0.0353(6)	0.0033(4)	0.0049(4)	0.0065(4)
C(13)	8*c*	0.2631(1)	0.1293(1)	0.57929(7)	0.0455(7)	0.0474(7)	0.0477(7)	0.0126(6)	0.0169(6)	0.0225(6)
C(14)	8*c*	0.3123(1)	0.1922(1)	0.63856(7)	0.0557(7)	0.0735(9)	0.0266(6)	0.0300(7)	0.0131(5)	0.0182(6)
C(15)	8*c*	0.3913(1)	0.2781(1)	0.62199(7)	0.0510(7)	0.0722(9)	0.0238(5)	0.0181(7)	–0.0015(5)	–0.0039(6)
C(16)	8*c*	0.4209(1)	0.3030(1)	0.54558(6)	0.0367(5)	0.0473(6)	0.0280(5)	0.0052(5)	–0.0008(4)	–0.0022(5)
C(21)	8*c*	0.33820(9)	0.35120(8)	0.36808(5)	0.0294(5)	0.0285(5)	0.0180(4)	0.0034(4)	0.0017(3)	–0.0002(3)
C(22)	8*c*	0.3992(1)	0.44361(9)	0.33870(6)	0.0330(5)	0.0342(5)	0.0281(5)	–0.0020(4)	0.0025(4)	0.0014(4)
C(23)	8*c*	0.3339(1)	0.52672(9)	0.30087(6)	0.0522(7)	0.0305(5)	0.0308(5)	0.0009(5)	0.0062(5)	0.0056(4)
C(24)	8*c*	0.2084(1)	0.5177(1)	0.29292(6)	0.0521(7)	0.0401(6)	0.0288(5)	0.0172(5)	–0.0009(5)	0.0059(5)
C(25)	8*c*	0.1480(1)	0.4256(1)	0.32202(7)	0.0318(5)	0.0503(7)	0.0360(6)	0.0094(5)	–0.0023(4)	0.0024(5)
C(26)	8*c*	0.21264(9)	0.34200(9)	0.35981(6)	0.0295(5)	0.0355(5)	0.0312(5)	0.0004(4)	0.0018(4)	0.0036(4)

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