Eric C. Hosten and Richard Betz*

Crystal structure of \(N, N\)-diphenylformamide, \(\text{C}_{13}\text{H}_{11}\text{NO}\)

https://doi.org/10.1515/ncrs-2020-0430
Received August 3, 2020; accepted September 23, 2020; published online October 5, 2020

Abstract
\(\text{C}_{13}\text{H}_{11}\text{NO}, \text{orthorhombic, Pca2}_1\) (no. 29), \(a = 23.801(4) \text{ Å}, b = 6.0510(13) \text{ Å}, c = 7.2677(14) \text{ Å}, V = 1046.7(3) \text{ Å}^3, Z = 4, R_{gt} = 0.0335, wR_{ref} (F^2) = 0.0896, T = 200 \text{ K}.

CCDC no.: 2033451

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: \(0.53 \times 0.41 \times 0.19 \text{ mm}\)
Wavelength: Mo Kα radiation (0.71073 Å)
\(\mu\): 0.08 mm\(^{-1}\)
Diffractometer, scan mode: Bruker APEX-II, \(\phi\) and \(\omega\)
\(\theta_{\text{max}}, \text{completeness}\): 28.0°, 99%
\(N(hk\bar{l})_{\text{measured}}, N(hk\bar{l})_{\text{unique}}, R_{\text{int}}\): 8805, 2435, 0.022
Criterion for \(I_{\text{obs}}, I(hk\bar{l})_{\text{gt}}\): \(I_{\text{obs}} > 2 \sigma(I_{\text{obs}}), 2215\)
\(N(\text{param})_{\text{refined}}\): 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.
Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

| Atom | x     | y     | z     | Ueq/ueq |
|------|-------|-------|-------|---------|
| 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   | 0.23763(8) | 0.2541(0) | 0.919125 | 0.057(4) |
| C11  | 0.10008(8) | 0.2313(3) | 0.9566(3) | 0.0338(4) |
| C12  | 0.0593(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 | 0.468611 | 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* |

1.433(2) Å and 1.437(2) Å, respectively, are slightly shorter than the most common values reported for C–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 C1(7)C1(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.

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

Research funding: R. Betz 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 and SAINT. Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.
2. Bruker. SADABS. Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
3. Sheldrick G. M. A short history of SHELX. Acta Crystallogr. 2008, A64, 112–122.
4. Farrugia L. J. WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. 2012, 45, 849–854.
5. 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.
6. Spek A. L. Structure validation in chemical crystallography. Acta Crystallogr. 2009, D65, 148–155.
7. Koz’mín P. A., Surazhskaya M. D., Larina T. B. Structure of Re$_2$Cl$_4$(HCOO)$_2$(HCON(C$_6$H$_5$)$_2$)$_2$ compound crystals. Koord. Khim. 1980, 6, 1259–1263.

8. Koz’mín P. A., Surazhskaya M. D., Larina T. B., Kotel’nikova A. S., Osmanov N. S. Synthesis and preliminary data on Re$_2$Cl$_4$(HCOO)$_2$(OCHN(C$_6$H$_5$)$_2$)$_2$ compound structure. Koord. Khim. 1979, 5, 1896–1897.

9. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. Acta Crystallogr. 2002, B58, 380–388.

10. Dorr M., Lips S., Martinez-Huithe C. A., Schollmeyer D., Franke R., Waldvogel S. R. Synthesis of highly functionalized N,N-diarylamides by an anodic C,N-coupling reaction. Chem. Eur. J. 2019, 25, 7835–7838.

11. Bernstein J., Davis R. E., Shimoni L., Chang N.-L. Patterns in hydrogen bonding: functionality and graph set analysis in crystals. Angew. Chem. Int. Ed. Engl. 1995, 34, 1555–1573.

12. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. Acta Crystallogr. 1990, B46, 256–262.