Eric C. Hosten and Richard Betz*

The crystal structure of 2,6-dimethyl-4-nitrophenol, $C_8H_9NO_3$

<https://doi.org/10.1515/ncrs-2020-0517>

Received October 3, 2020; accepted October 30, 2020;

published online November 16, 2020

Abstract

$C_8H_9NO_3$, monoclinic, $P2_1/n$ (no. 14), $a = 6.9121(4)$ Å, $b = 26.9700(15)$ Å, $c = 8.7204(5)$ Å, $\beta = 106.152(3)^\circ$, $V = 1561.48(16)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0486$, $wR_{ref}(F^2) = 0.1399$, $T = 200$ K.

CCDC no.: 2041501

The asymmetric unit of the title crystal 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.

Table 1: Data collection and handling.

Crystal:	Brown block
Size:	$0.59 \times 0.41 \times 0.17$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.0° , 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14532, 3742, 0.022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2926
$N(\text{param})_{\text{refined}}$:	223
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Source of material

The compound was obtained commercially (Sigma-Aldrich). Crystals suitable for the 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 for aromatic carbon atoms) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

*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>

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O11	0.67537 (19)	0.21527 (4)	0.03311 (13)	0.0302 (3)
H11	0.661069	0.238507	−0.033258	0.045*
O111	0.6531 (2)	0.32573 (5)	0.65794 (15)	0.0406 (3)
O112	0.6444 (2)	0.24915 (5)	0.72876 (14)	0.0374 (3)
N11	0.6507 (2)	0.28120 (5)	0.62934 (15)	0.0271 (3)
C11	0.6667 (2)	0.23360 (6)	0.17562 (17)	0.0223 (3)
C12	0.6667 (2)	0.28464 (5)	0.20649 (17)	0.0217 (3)
C13	0.6613 (2)	0.29998 (5)	0.35705 (17)	0.0225 (3)
H13	0.661837	0.334309	0.381509	0.027*
C14	0.6550 (2)	0.26486 (6)	0.47146 (17)	0.0221 (3)
C15	0.6562 (2)	0.21431 (5)	0.44144 (18)	0.0235 (3)
H15	0.653078	0.191127	0.522735	0.028*
C16	0.6618 (2)	0.19789 (5)	0.29200 (18)	0.0239 (3)
C17	0.6768 (3)	0.32154 (6)	0.07992 (19)	0.0285 (3)
H17A	0.671266	0.355222	0.120653	0.043*
H17B	0.562660	0.316375	−0.014679	0.043*
H17C	0.803089	0.317098	0.051216	0.043*
C18	0.6669 (3)	0.14370 (6)	0.2539 (2)	0.0346 (4)
H18A	0.657725	0.124060	0.346147	0.052*
H18B	0.793371	0.135978	0.228903	0.052*
H18C	0.553056	0.135681	0.161710	0.052*
O21	0.7393 (2)	0.03939 (4)	0.55281 (13)	0.0314 (3)
H21	0.749532	0.015997	0.491925	0.047*
O211	0.7520 (2)	0.00439 (5)	1.25827 (13)	0.0360 (3)
O212	0.7673 (2)	−0.07191 (5)	1.18716 (15)	0.0400 (3)
N21	0.7572 (2)	−0.02739 (5)	1.15789 (15)	0.0260 (3)
C21	0.7428 (2)	0.02095 (5)	0.69844 (16)	0.0217 (3)
C22	0.7296 (2)	0.05633 (5)	0.81357 (17)	0.0222 (3)
C23	0.7337 (2)	0.03953 (5)	0.96466 (17)	0.0221 (3)
H23	0.725179	0.062450	1.045238	0.026*
C24	0.7503 (2)	−0.01072 (5)	0.99783 (16)	0.0210 (3)
C25	0.7643 (2)	−0.04561 (5)	0.88416 (17)	0.0222 (3)
H25	0.775612	−0.079876	0.910323	0.027*
C26	0.7617 (2)	−0.02994 (5)	0.73230 (17)	0.0217 (3)
C27	0.7126 (3)	0.11043 (6)	0.7724 (2)	0.0334 (4)
H27A	0.585329	0.116573	0.690713	0.050*
H27B	0.825371	0.120276	0.731502	0.050*
H27C	0.715958	0.129805	0.868220	0.050*
C28	0.7808 (3)	−0.06648 (6)	0.60658 (19)	0.0306 (4)
H28A	0.789721	−0.100168	0.650124	0.046*
H28B	0.902514	−0.059108	0.574113	0.046*
H28C	0.662470	−0.063932	0.513748	0.046*

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 in the *SHELX* program suite [3]), with *U*(H) set to 1.5*U*_{eq}(C).

The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to best fit the

experimental electron density (HFIX 147 in the *SHELX* program suite [3]), with *U*(H) set to 1.5*U*_{eq}(O).

Comment

Phenols are interesting bonding partners for a variety of transition metals and elements from the p-block of the periodic system. They can act as neutral or – upon deprotonation – as anionic monodentate ligands. Upon variation of the substituents on the aromatic system, a seemingly endless series of symmetric as well as asymmetric phenol derivatives featuring different steric pretenses and acidities of the hydroxyl-group are available. For phenol and phenolate, all bonding modes from monodentate (e.g. towards beryllium [7]) via bidentate (e.g. towards tin [8]) and tridentate (e.g. towards zinc [9, 10]) to tetradentate (e.g. towards sodium [11]) have been observed and secured based on structural studies conducted on single crystals. In continuation of our interest in structural features of derivatives of phenol [12–16] the molecular and crystal structure of the title compound was elucidated.

The title structure proves the presence of a phenol derivative bearing two methyl groups in *ortho* position to the hydroxyl group as well as nitro group in *para* position to the protic substituent. The asymmetric unit contains two complete molecules (see the figure). C–N bond lengths of 1.4537(18) and 1.4546(18) Å as well as C–O bond distances of 1.3542(17) and 1.3578(17) Å are in good agreement with other nitro- and hydroxy-substituted compounds whose structures have been deposited with the Cambridge Structural Database [17]. Both molecules are essentially flat as the least-squares planes defined by their respective non-hydrogen atoms show maximum deviations of only 0.022(2) and 0.033(2) Å respectively (invariably for one of the exocyclic carbon atoms) – a finding that can be rationalized on grounds of extensive resonance stabilization that engulfs the substituents able to partake in it. The two molecules are further almost co-planar as the least-squares planes as just defined enclose an angle of 5.40(4)° only.

In the crystal, classical hydrogen bonds of the O–H···O type are observed next to C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. The classical hydrogen bonds employ one of the oxygen atoms of the nitro group in a symmetry-generated equivalent of the atom bearing the donating O–H group as acceptor. In contrast to this,

the C–H...O contacts – invariably supported by one hydrogen atom on one of the methyl substituents each – seek the remaining oxygen atom of the nitro group in the other molecule present in the asymmetric unit as acceptor. In terms of graph-set analysis [18, 19], the descriptor for the classical hydrogen bonds is $C_1^1(8)C_1^1(8)$ on the unary level while the C–H...O contacts necessitate a $R_2^2(14)R_2^2(14)$ on the binary level. In total, the two molecules present in the asymmetric unit are connected to strands along the crystallographic c axis. The crystal structure is further characterized by π stacking interactions with the shortest distance between two centers of gravity measured at only 3.7608(8) Å.

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

Research funding: National Research Foundation.

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

References

1. Bruker. *APEX2*; 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., Rodríguez-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. Arrowsmith M., Hill M. S., Kociok-Kohn G., MacDougall D. J., Mahon M. F., Mallov I. Three-coordinate beryllium β -diketiminates: synthesis and reduction chemistry. *Inorg. Chem.* 2012, *51*, 13408–13418.
8. Yasuda H., Choi J.-C., Lee S.-C., Sakakura T. Structure of dialkyltin diaryloxides and their reactivity toward carbon dioxide and isocyanate. *J. Organomet. Chem.* 2002, *659*, 133–141.
9. Boersma J., Spek A. L., Noltes J. G. Coordination complexes of bis(2,2-dimethyl-3,5-hexanedionato) zinc with organozinc-oxygen and -nitrogen compounds. crystal structure of the complex formed with phenylzinc phenoxide. *J. Organomet. Chem.* 1974, *81*, 7–15.
10. Enthaler S., Eckhardt B., Inoue S., Irran E., Driess M. Facile and efficient reduction of ketones in the presence of zinc catalysts modified by phenol ligands. *Chem. Asian J.* 2010, *5*, 2027–2035.
11. Kunert M., Dinjus E., Nauck M., Sieler J. Structure and reactivity of sodium phenoxide – following the course of the Kolbe–Schmitt reaction. *Chem. Ber.* 1997, *130*, 1461–1465.
12. Habarurema G., Gerber T. I. A., Hosten E., Betz R. Redetermination of the crystal structure of 2,6-diformyl-4-methylphenol, at 200 K, $C_9H_8O_3$. *Z. Kristallogr. NCS* 2014, *229*, 331–332.
13. Betz R., McClelland C., Marchand H. Redetermination of 3,5-dimethylphenol. *Acta Crystallogr.* 2011, *C67*, o1152.
14. Betz R., Klüfers P., Mayer P. 2,3,4,5,6-Pentabromophenol. *Acta Crystallogr.* 2008, *E64*, o1921.
15. Betz R., Klüfers P., Mayer P. 4-Ethylphenol. *Acta Crystallogr.* 2009, *E65*, o544.
16. Manana P., Cuthbertson J., Hosten E. C., Betz R. The crystal structure of 2,6-difluorophenol, $C_6H_4F_2O$. *Z. Kristallogr. NCS*. accepted.
17. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
18. 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.
19. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.