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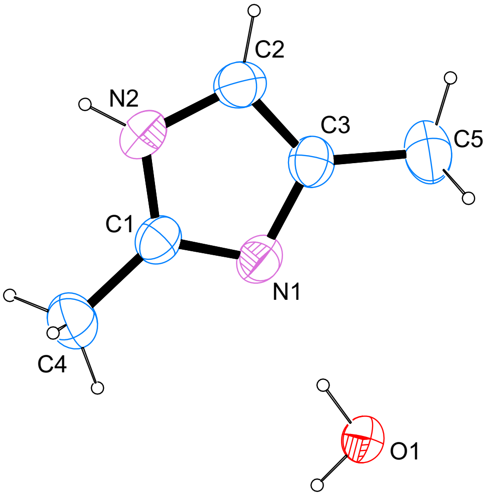
The crystal structure of 2,4-dimethylimidazole monohydrate, $C_5H_{10}N_2O$



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Abstract

$C_5H_{10}N_2O$, monoclinic, Ia (no. 9), $a = 4.7212(4)$ Å, $b = 11.1424(8)$ Å, $c = 12.8211(9)$ Å, $\beta = 94.349(3)°$, $V = 672.52(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0280$, $wR_{ref}(F^2) = 0.0821$, $T = 200$ 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 (Aldrich). Crystals suitable for the diffraction study were taken directly from the provided product.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.55 × 0.42 × 0.22 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	3023, 1582, 0.010
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1557
$N(param)_{refined}$:	88
Programs:	Bruker [1, 2], SHELX [3], WinGX/ ORTEP [4], Mercury [5], PLATON [6]

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

Atom	x	y	z	$U_{iso}*/U_{eq}$
N1	0.5153 (2)	0.71437 (11)	0.51093 (10)	0.0380 (3)
N2	0.5133 (2)	0.81707 (12)	0.65708 (10)	0.0393 (3)
H2A	0.472 (5)	0.839 (2)	0.717 (2)	0.059 (7)*
C1	0.4111 (3)	0.71980 (12)	0.60389 (11)	0.0360 (3)
C2	0.6901 (3)	0.87642 (13)	0.59414 (13)	0.0422 (3)
H2	0.792360	0.948236	0.610629	0.051*
C3	0.6908 (3)	0.81291 (14)	0.50409 (11)	0.0381 (3)
C4	0.2098 (4)	0.63294 (15)	0.64498 (14)	0.0482 (4)
H4A	0.056739	0.676547	0.676052	0.072*
H4B	0.310313	0.582509	0.698370	0.072*
H4C	0.129063	0.582293	0.587710	0.072*
C5	0.8447 (4)	0.8372 (2)	0.40854 (15)	0.0543 (4)
H5A	0.706676	0.851559	0.348855	0.081*
H5B	0.962909	0.767831	0.393875	0.081*
H5C	0.965501	0.908214	0.420304	0.081*
O1	0.4029 (2)	0.56654 (9)	0.34354 (8)	0.0373 (3)
H1A	0.246 (6)	0.530 (2)	0.3499 (19)	0.051 (6)*
H1B	0.421 (6)	0.611 (2)	0.400 (2)	0.062 (7)*

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 $U(H)$ set to $1.2U_{eq}(C)$.

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

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experimental electron density (HFIX 137 in the *SHELX* program suite [3]), with $U(\mathrm{H})$ set to $1.5U_{\mathrm{eq}}(\mathrm{C})$.

The H atoms of the water molecule as well as the nitrogen-bound H atom were located on a difference Fourier map and refined freely.

Given the space group is non-centrosymmetric, the structure was formally refined as an inversion twin with a volume ratio of 73.4:26.6.

Due to the absence of a strong anomalous scatterer, the Flack parameter is meaningless. Thus, the item was removed from the CIF.

Comment

Synthesis and analysis are the two major aspects of historic and contemporary chemistry. For a large variety of reactions well-established standard synthesis procedures are apparent that form the basis of vast sections of practical laboratory courses during undergraduate student training. Against this backdrop it then seems improbable that one specific synthesis reaction (whose nature is known and understood) would then – all of a sudden – yield surprising results contradicting experience. The latter is a particularly suspicious development if the unexpected results coincide with a change in reagent supply as the historic example of the Simmons–Smith reaction has shown when success or failure during the early years of this reaction being applied could be attributed to the catalytic effects of silver present in one of the starting materials [7–11]. In our case, coordination reactions involving 2,4-dimethylimidazole as a ligand started providing unexpected results indicative of partial hydrolysis reactions. As the onset of the changed behaviour coincided with an older batch of the reagent being used in our laboratories, the nature of the compound was checked by means of a diffraction study. Structural information about the title compound acting as a cation is apparent in the literature [12, 13].

The structure solution shows a surprising picture. Apart from the expected dimethylated heterocycle one molecule of water is present in the asymmetric unit. C–N bond lengths of 1.3250(17) and 1.382(2) Å for the imine-type nitrogen atom and 1.3501(19) and 1.374(2) Å for the amine-type nitrogen atom are in good agreement with values found for other imidazole derivatives whose metrical parameters have been deposited with the Cambridge Structural Database [14]. The molecule is essentially planar with the largest deviation found for the least-squares plane as defined by the non-hydrogen atoms of the heterocycle measured at 0.340(8) Å for the intracyclic carbon atom bearing one of the methyl groups and bonding to only one of the two pnicogen atoms.

In the crystal, classical hydrogen bonds of the O–H⋯O and O–H⋯N type are observed next to N–H⋯O ones. The water molecules form a cooperative chain of hydrogen bonds with one of its protons while the second proton uses the imine-type nitrogen atom as acceptor. In terms of graph-set analysis [15, 16], the descriptor for these bonds is $DDC_1^1(2)$ on the unary level. In total, the entities within the crystal are connected to a three-dimensional network with the water molecules lined up along the crystallographic *a* axis. A potential C–H⋯π interaction supported by one of the methyl group hydrogen atoms can be neglected on grounds of its C–H⋯π angle deviating considerably from a linear configuration with a value of just 129°. π stacking is not a prominent stabilizing feature in the crystal structure of the title compound as the shortest distance in between two centers of gravity was measured at 4.7212(9) Å.

The results of this study strengthen the notion that even simple, solid organic compounds that enjoy a – supposedly! – infinite shelf-live and are impervious to decomposition can undergo chemical alterations over prolonged storage.

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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., 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. Simmons H. E. Jr., Smith R. D. A new synthesis of cyclopropanes from olefins. *J. Am. Chem. Soc.* 1958, *80*, 5323–5324.
8. Simmons H. E., Smith R. D. A new synthesis of cyclopropanes. *J. Am. Chem. Soc.* 1959, *81*, 4256–4264.
9. Denis J. M., Girard J. M., Conia J. M. Improved Simmons–Smith reactions. *Synthesis* 1972, *10*, 549–551.

10. Charette A. B., Beauchemin A. Simmons-Smith cyclopropanation reaction. *Org. React.* 2004, *58*, 1–415.
11. Lévesque E., Goudreau S. R., Charette A. B. Improved zinc-catalyzed Simmons–Smith reaction: access to various 1,2,3-trisubstituted cyclopropanes. *Org. Lett.* 2014, *16*, 1490–1493.
12. Wang L., Hu Y., Xu W., Pang Y., Liu F., Yang Y. Investigation of hydrogen bonding patterns in a series of multi-component molecular solids formed by tetrabromoterephthalic acid with selected *N*-heterocycles. *RSC Adv.* 2014, *4*, 56816–56830.
13. Boeer A. B., Collison D., Muryn C. A., Timco G. A., Tuna F., Winpenny R. E. P. Linkage isomerism and spin frustration in heterometallic rings: synthesis, structural characterization, and magnetic and EPR spectroscopic studies of Cr_7Ni, Cr_6Ni_2, and Cr_7Ni_2 rings templated about imidazolium cations. *Chem. Eur. J.* 2009, *15*, 13150–13160.
14. Allen F. H. The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr.* 2002, *B58*, 380–388.
15. 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.
16. Etter M. C., MacDonald J. C., Bernstein J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* 1990, *B46*, 256–262.