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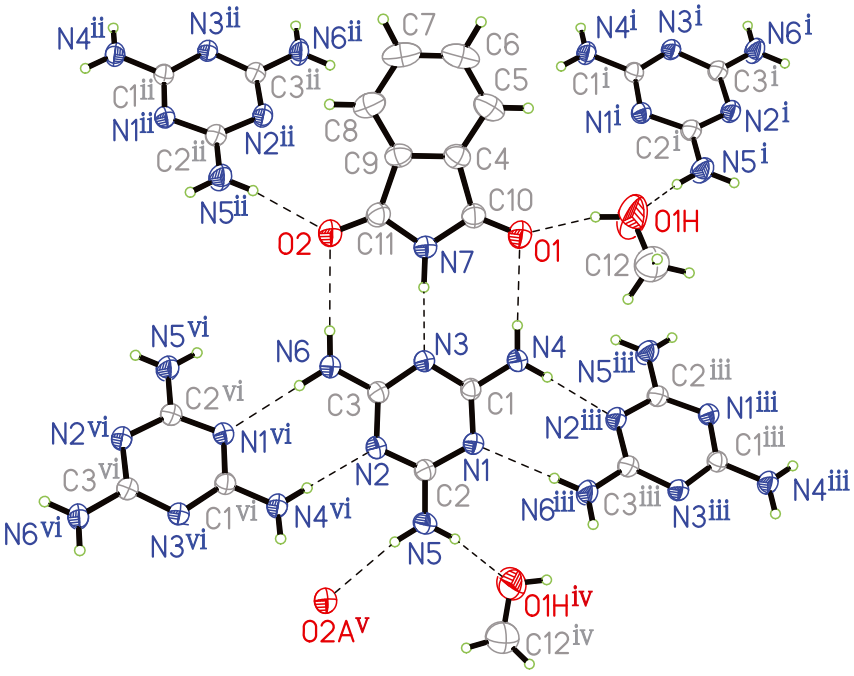
Crystal structure of the cocrystal 2,4,6-triamino-1,3,5-triazine – 1*H*-isoindole-1,3(2*H*)-dione – methanol (1/1/1), $C_{12}H_{15}N_7O_3$



https://doi.org/10.1515/ncrs-2022-0261
Received May 20, 2022; accepted June 8, 2022;
published online July 12, 2022

Abstract

$C_{12}H_{15}N_7O_3$, $P2_1/c$ (no. 14), a = 7.1782(3) Å, b = 16.6800(6) Å, c = 12.1070(5) Å, β = 92.030(2)°, V = 1448.69(10) Å^3, Z = 4, $R_{gt}(F)$ = 0.0449, $wR_{ref}(F^2)$ = 0.1220, T = 296(2) K.

CCDC no.: 2182446

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.20 × 0.20 × 0.20 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	0.89 mm^{-1}
Diffractometer, scan mode:	Bruker APEX3, φ and ω
θ_{max}, completeness:	72.2°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12,956, 2788, 0.044
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2451
N(param)$_{refined}$:	215
Programs:	Bruker [1], Shelx [2, 3]

The molecular structure is shown in the figure (symmetry code i) $-x + 1$, $y - 0.5$, $-z + 1.5$; ii) $-x + 1$, $y - 0.5$, $-z + 0.5$; iii) x, $-y + 1.5$, $z + 0.5$; iv) $-x + 1$, $y + 0.5$, $-z + 1.5$; v) $-x + 1$, $y + 0.5$, $-z + 0.5$; vi) x, $-y + 1.5$, $z - 0.5$). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.77763 (18)	0.48446 (7)	0.63688 (9)	0.0495 (3)
O2	0.73763 (17)	0.47187 (7)	0.26140 (9)	0.0472 (3)
N1	0.48553 (16)	0.76466 (7)	0.54272 (9)	0.0316 (3)
N2	0.48105 (17)	0.76418 (7)	0.34500 (9)	0.0347 (3)
N3	0.57738 (16)	0.64749 (7)	0.44564 (9)	0.0308 (3)
N4	0.58375 (17)	0.65188 (7)	0.63506 (9)	0.0359 (3)
H4A	0.565381	0.676383	0.696222	0.043*
H4B	0.624555	0.603403	0.635834	0.043*
N5	0.3781 (2)	0.87190 (8)	0.44225 (11)	0.0452 (4)
H5B	0.357019	0.895889	0.503428	0.054*
H5C	0.353090	0.895498	0.380335	0.054*
N6	0.5735 (2)	0.65050 (8)	0.25636 (10)	0.0473 (4)
H6B	0.613390	0.601880	0.257049	0.057*
H6C	0.553089	0.674837	0.194484	0.057*
N7	0.74011 (18)	0.49566 (8)	0.44844 (10)	0.0378 (3)
H7N	0.685 (3)	0.5476 (14)	0.4445 (17)	0.062 (6)*
C1	0.54889 (17)	0.68916 (8)	0.53879 (10)	0.0280 (3)
C2	0.44947 (19)	0.79830 (8)	0.44339 (11)	0.0313 (3)
C3	0.54331 (19)	0.68818 (8)	0.35128 (11)	0.0313 (3)
C4	0.87601 (19)	0.37945 (9)	0.51090 (12)	0.0364 (3)
C5	0.9523 (2)	0.31777 (10)	0.57374 (16)	0.0479 (4)
H5A	0.961700	0.320866	0.650429	0.057*
C6	1.0140 (2)	0.25114 (11)	0.51753 (19)	0.0561 (5)
H6A	1.066654	0.208632	0.557333	0.067*
C7	0.9991 (3)	0.24635 (11)	0.40369 (19)	0.0578 (5)
H7A	1.040814	0.200497	0.368521	0.069*
C8	0.9231 (2)	0.30867 (10)	0.34058 (16)	0.0490 (4)
H8A	0.913054	0.305583	0.263902	0.059*
C9	0.8635 (2)	0.37513 (9)	0.39665 (13)	0.0367 (3)
C10	0.7951 (2)	0.45710 (9)	0.54442 (12)	0.0360 (3)
C11	0.7750 (2)	0.45069 (9)	0.35583 (12)	0.0359 (3)
O1H	0.7746 (4)	0.46085 (12)	0.87128 (14)	0.1113 (8)
H1H	0.764 (5)	0.457 (2)	0.797 (4)	0.134*
C12	0.8271 (4)	0.53823 (16)	0.8936 (2)	0.0783 (7)
H12A	0.811 (5)	0.549 (2)	0.973 (3)	0.117*
H12B	0.752 (5)	0.579 (2)	0.850 (3)	0.117*
H12C	0.965 (5)	0.5445 (19)	0.883 (3)	0.117*

Source of material

2,4,6-Triamino-1,3,5-triazine (melamine) mono(dimethyl sulfoxide) solvate (MA-DMSO) was prepared by following the literature procedures [4]. MA-DMSO (25 mg, 0.198 mmol) was dissolved in methanol (12 mL) under reflux at 70 °C under N_2 atmosphere to obtain a clear solution. To 4.0 mL of the solution, 29.2 mg (0.198 mmol) of 1*H*-isoindole-1,3(2*H*)-dione (phthalimide) was added. The mixture was kept at 50 °C to get a clear solution and was then cooled down naturally. Crystals of the title compound suitable for single crystal analysis were obtained in 2–3 days, with a yield of 12.5 mg or 50%.

Experimental details

A crystal of a size 0.20 × 0.20 × 0.20 mm was mounted on a glass fiber with expoxy glue. Data collection was performed on a Bruker D8 VENTURE Photon II diffractometer at room temperature, operating at 50 kV and 30 mA. Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package [1]. Data collection: Bruker APEX3; cell refinement: Bruker SAINT; Data reduction: Bruker SAINT; Structure solution: Shelxt 2014/5 [2]; Structure refinement: Shelxl-2018/3 [3]; Molecular graphics: Bruker Shelxtl [2]; Publication materials: Bruker Shelxtl [2].

The H-atoms on N7 and O1H were located from the difference-Fourier maps. All other H-atoms were placed geometrically and refined using a riding model with common isotropic displacement factors $U_{iso}(H) = 1.2\,U_{eq}$ (parent C-atom).

Comment

The development of multipoint hydrogen bonding motifs that form complexes or cocrystals with high stability and selectivity is important both for the understanding of biological processes and in the design of new materials [5]. In the study of organic semiconductors, the key materials of today's organic electronics, hydrogen bonding have received surprisingly limited, but quickly growing attentions [6, 7]. Efficient charge transport in hydrogen-bonded materials has been realized in organic field-effect transistor (OFET) devices, where the organic complex or cocrystal serves as an active layer across extraordinary charge pathways, ensuring the efficient transport of induced charges [8–11]. Naphthalenetetracarboxydiimide and its derivatives (NDIs) and related arylenetetracarboxydiimides are among the most promising candidates of next generation n-type organic semiconductors, with their electronic properties being easily tailored through π- and/or N-substitutions [12–14]. For examples, not only they show record-high electron mobilities in organic field electric transistors (OFETs), but also they are only second to fullerene derivatives when used in OPV as the acceptor. Meanwhile, the electronic properties of NDIs can be tuned through strong H-bonding interactions [15, 16].

With an Acceptor–Donor–Acceptor (ADA) structure, naphthalenetetracarboxydiimide (NDI) can triply hydrogen-bond to a compound with a complimentary structure, i.e. Donor–Acceptor–Donor (DAD) structure, such as 2,4-diaminopyridine or 2,4,6-triamino-1,3,5-triazine (melamine). However, since the structure of NDI is quite

rigid, it has limited solubility in most of the solvents, which makes co-crystal production in solution very challenging. We therefore use 1*H*-isoindole-1,3(2*H*)-dione (phthalimide) as a model compound to study its co-crystallization reaction with melamine and the ADA…DAD triply hydrogen bonding. It is worth noting that, by reacting phthalimide (PI) and melamine (MA) via a gaseous phase reaction, a co-crystal compound, $(MA)(PI)_3$ had been obtained [17].

The asymmetric unit contains one 2,4,6-triamino-1,3,5-triazine molecule (melamine: MA), one 1*H*-isoindole-1,3(2*H*)-dione molecule and one methanol solvent molecule (see the figure). All moieties are connected by hydrogen bonds to form the title cocrystal. The structure demonstrates a polymeric feature with each MA hydrogen-bonded to two neighboring MA molecules, two isoindoles and two methanol molecules. All bond lengths are in the expected ranges.

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

Research funding: This work is supported by Key Program Special Fund of XJTLU (Research Project No. KSF-E-06).

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

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