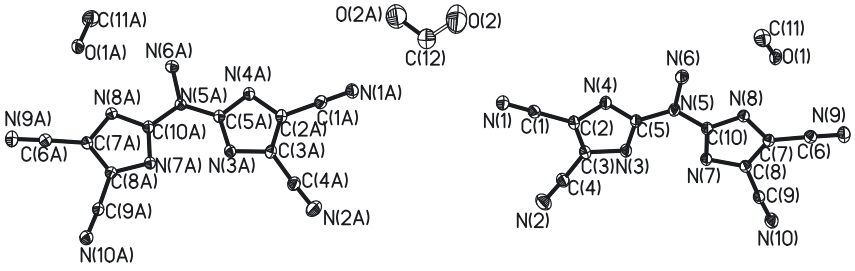
Zhang Yuyao, Wang Bo, Fan Shengping and Li Yunlu*

The cocrystal of 2,2′-(hydrazine-1,1-diyl)bis(1*H*-imidazole-4,5-dicarbonitrile)– methanol (2/3)



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Abstract

$C_{23}H_{20}N_{20}O_3$, monoclinic, $C2/c$ (no. 15), a = 21.738(2) Å, b = 6.0988(9) Å, c = 24.229(3) Å, β = 114.396(4)°, V = 2,925.3(7) Å^3, Z = 4, $R_{gt}(F)$ = 0.0533, $wR_{ref}(F^2)$ = 0.1434, T = 170 K.

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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:	Colourless block
Size:	0.12 × 0.10 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.4°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11,927, 2,945, 0.054
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,978
$N(param)_{refined}$:	217
Programs:	Olex2,[1] SHELX,[2,3] Bruker[4]

1 Source of material

An appropriate amount of 2-amino-4,5-dicyan-imidazole, hydrochloric acid and potassium permanganate were added to the reactor. The temperature of the reactor was reduced to 273 K and the reactions are for 2 h. After the end of the reaction, the solids are removed and the filtrate is retained. The solvent in the filtrate is removed by a rotary evaporator to obtain white solid. The white solid was separated by column chromatography using petroleum ether and ethyl acetate as eluent. The solution obtained by column chromatography was evaporated at room temperature to obtain the colorless block shaped crystals.

2 Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

3 Comment

Azole heterocyclic compounds are a class of high-energy nitrogen-rich energetic materials.[5,6] Imidazole compounds are currently the focus of research on field of energetic materials due to good thermal stability and a large number of modification sites.[7–9]

The title compound is cocrystal of two 2,2′-(hydrazine-1,1-diyl)bis(1H-imidazole-4,5-dicarbonitrile) molecules and three methanol molecules. The bond lengths and angles are in the expected ranges. 2,2′-(hydrazine-1,1-diyl)bis (1h-imidazole-4,5-dicarbonitrile) molecules are formed by connecting two

***Corresponding author: Li Yunlu**, School of Environment and Safety Engineering, North University of China, Taiyuan 030051, Shanxi Province, P.R. China, E-mail: liyunlu2014@163.com. https://orcid.org/0000-0003-1998-4292
Zhang Yuyao, School of Environment and Safety Engineering, North University of China, Taiyuan 030051, Shanxi Province, P.R. China. https://orcid.org/0009-0008-9973-3242
Wang Bo and Fan Shengping, Subunit 51 of 32272nd Unit of the Chinese People's Liberation Army, Yuzhong 730100, Gansu Province, P.R. China

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.67157 (11)	0.4163 (4)	0.73264 (11)	0.0323 (5)
C2	0.70122 (11)	0.3454 (4)	0.69247 (10)	0.0313 (5)
C3	0.68488 (11)	0.1616 (4)	0.65693 (10)	0.0313 (5)
C4	0.63782 (13)	−0.0079 (4)	0.65031 (11)	0.0368 (6)
C5	0.76419 (11)	0.3498 (4)	0.64570 (10)	0.0303 (5)
C6	0.92554 (12)	0.2379 (4)	0.49950 (11)	0.0343 (6)
C7	0.88132 (11)	0.2200 (4)	0.52903 (10)	0.0298 (5)
C8	0.83496 (11)	0.0622 (4)	0.52438 (10)	0.0297 (5)
C9	0.82047 (12)	−0.1274 (4)	0.48685 (11)	0.0336 (6)
C10	0.83010 (11)	0.2982 (4)	0.58628 (10)	0.0298 (5)
C11	0.98614 (14)	0.8603 (5)	0.64197 (13)	0.0532 (8)
H11A	1.0118	0.9793	0.6342	0.080*
H11B	1.0166	0.7705	0.6758	0.080*
H11C	0.9507	0.9224	0.6523	0.080*
N1	0.64750 (10)	0.4727 (4)	0.76410 (10)	0.0388 (5)
N2	0.59870 (12)	−0.1397 (4)	0.64588 (12)	0.0539 (7)
N3	0.72580 (9)	0.1678 (3)	0.62602 (8)	0.0308 (5)
H3	0.7267	0.0728	0.5990	0.037*
N4	0.75134 (9)	0.4644 (3)	0.68592 (9)	0.0333 (5)
N5	0.81237 (10)	0.4150 (3)	0.62595 (9)	0.0355 (5)
N6	0.84711 (11)	0.6146 (4)	0.64618 (11)	0.0433 (6)
H6A	0.8178	0.7233	0.6355	0.052*
H6B	0.8684	0.6105	0.6860	0.052*
N7	0.80248 (9)	0.1103 (3)	0.56099 (9)	0.0309 (5)
N8	0.87794 (9)	0.3720 (3)	0.56936 (9)	0.0307 (5)
H8	0.9020	0.4926	0.5816	0.037*
N9	0.95963 (12)	0.2476 (4)	0.47445 (11)	0.0479 (6)
N10	0.80961 (11)	−0.2748 (4)	0.45454 (10)	0.0425 (6)
O1	0.95627 (8)	0.7281 (3)	0.58934 (8)	0.0438 (5)
H1	0.9818	0.7239	0.5711	0.066*
O2[a]	0.5482 (4)	0.9200 (13)	0.7450 (5)	0.146 (3)
H2[a]	0.5481	1.0461	0.7589	0.219*
C12	0.5000	0.8006 (10)	0.7500	0.0811 (16)
H12A[a]	0.4587	0.8116	0.7125	0.122*
H12B[a]	0.4911	0.8545	0.7841	0.122*
H12C[a]	0.5145	0.6471	0.7571	0.122*

[a]Occupancy: 0.5.

imidazole planes by –N–NH_2 structure. The two imidazole planes form a small angle and the dihedral angle is only 1.637°. Four hydrogen bonds are formed within 2,2′-(hydrazine-1,1-diyl)bis(1H-imidazole-4,5-dicarbonitrile) molecules. The bond lengths of hydrogen bonds are 2.696, 2.745, 2.441 and 2.207 respectively. The four carbon atoms of C2, C3, C7 and C8 are connected with four –CN groups and each –C–CN triatom structure is collinear. The above collinear structure is the same as the structure of 2-amino-4,5-dicyan-imidazole.[10]

2,2′-(Hydrazine-1,1-diyl)bis(1h-imidazole-4,5-dicarbonitrile) is synthesized from two 2-amino-4,5-dicarbonitrile molecules. During the reaction, the amino group of one 2-amino-4,5-dicarbonitrile molecule is removed, and two hydrogen atoms of another 2-amino-4, 5-dicyanimidazole is removed. The two intermediates are connected by nitrogen atom and the free amino groups is attached to nitrogen atom, forming 2,2′-(hydrazine-1,1-diyl)bis(1h-imidazole-4,5-dicarbonitrile) molecule.

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

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

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References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
2. Sheldrick, G. M. *SHELXTL* – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. BRUKER. *SAINT*, *APEX2 and SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2016.
5. Su, P.; Song, X.; Sun, R. Hydrogen Bonding in the Crystal Structure of the Molecular Salt of Pyrazole–Pyrazolium Picrate. *Acta Crystallogr.* **2016**, *E72*, 861–863.
6. Matuszek, K.; Vijayaraghavan, R.; Forsyth, C. M. Pyrazolium Phase Change Materials for Solar-Thermal Energy Storage. *ChemSusChem* **2019**, *13*, 201902601.
7. Tan, Y.; Yang, Z.; Wang, H. High Energy Explosive with Low Sensitivity: A New Energetic Cocrystal Based on CL-20 and 1,4–DNI. *Cryst. Growth Des.* **2019**, *19*, 4476–4482.
8. Windler, G. K.; Scott, B. L.; Tomson, N. C. Crystal Structure of 4,5-Dinitro-1*H*-Imidazole. *Acta Crystallogr.* **2015**, *E71*, o634.
9. Marcin, S.; Hines, C. C.; Reichert, W. M. Azolium Azolates from Reactions of Neutral Azoles with 1,3-Dimethyl-Imidazolium-2-Arboxylate, 1,2,3-Trimethyl-Imidazolium Hydrogen Carbonate, and N,N-Dimethyl-Pyrrolidinium Hydrogen Carbonate. *New J. Chem.* **2013**, *37*, 1461–1469.
10. Hardgrove, G. L. Jnr; Jons, S. D. Structure of 2-Amino-4,5-Dicyanoimidazole. *Acta Crystallogr.* **1991**, *C47*, 337–339.