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Crystal structure of 5-(4-(1*H*-tetrazol-5-yl)phenyl)-1*H*-imidazol-3-ium 7-carboxy-1,3-dioxo-1*H*,3*H*-benzo[*de*]isochromene-6-carboxylate monohydrate 4,5-anhydride, C₂₄H₁₆N₆O₈

Table 1: Data collection and handling.

Crystal:	Colourless needle
Wavelength:	Size 0.26 × 0.21 × 0.18 mm
μ :	Mo $K\alpha$ radiation (0.71073 Å)
Diffractometer, scan mode:	1.2 cm ⁻¹
2 θ _{max} , completeness:	Bruker SMART, φ and ω
$N(hkl)$ _{measured} , $N(hkl)$ _{unique} , R_{int} :	56.8°, >99%
Criterion for I_{obs} , $N(hkl)_{gt}$:	15349, 5365, 0.033
$N(param)_{refined}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3727
Programs:	367
	Bruker programs [10], SHELX [11]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C1	0.9775(2)	0.15983(7)	0.2801(2)	0.0418(5)
H1	1.0570	0.1361	0.2821	0.050*
C2	0.8689(2)	0.14650(7)	0.3411(2)	0.0394(4)
H2	0.8772	0.1141	0.3851	0.047*
C3	0.7479(2)	0.18123(7)	0.3366(2)	0.0374(4)
C4	0.7401(3)	0.22992(8)	0.2734(3)	0.0579(6)
H4	0.6599	0.2536	0.2704	0.070*
C5	0.8491(3)	0.24358(8)	0.2153(3)	0.0566(6)
H5	0.8434	0.2766	0.1748	0.068*
C6	0.9682(2)	0.20826(7)	0.2166(2)	0.0405(4)
C7	1.0816(2)	0.22242(7)	0.1513(2)	0.0412(4)
C8	0.6309(2)	0.16930(7)	0.3999(2)	0.0368(4)
C9	0.5171(2)	0.20060(8)	0.4160(2)	0.0451(5)
H9	0.4950	0.2352	0.3861	0.054*
C10	0.5037(3)	0.12486(8)	0.5098(2)	0.0462(5)
H10	0.4721	0.0979	0.5547	0.055*
C11	0.8313(2)	0.09323(7)	−0.0673(2)	0.0357(4)
C12	0.8035(2)	0.06284(6)	0.04371(18)	0.0299(4)
C13	0.65633(19)	0.06859(6)	0.06306(17)	0.0272(3)
C14	0.5385(2)	0.10438(6)	−0.02162(18)	0.0315(4)
C15	0.5733(2)	0.13782(7)	−0.1231(2)	0.0367(4)
C17	0.9214(2)	0.03010(7)	0.12865(19)	0.0341(4)
H17	1.0153	0.0251	0.1122	0.041*
C18	0.9010(2)	0.00396(7)	0.24069(19)	0.0340(4)
H18	0.9842	−0.0171	0.3004	0.041*
C19	0.7610(2)	0.00868(6)	0.26482(18)	0.0294(4)

DOI 10.1515/ncrs-2016-0095

Received March 27, 2016; accepted July 12, 2016; available online August 10, 2016

Abstract

C₆H₂₅Br₃N₂O₃P₂, monoclinic, $P2_1/c$ (no. 14), $a = 8.9705(10)$ Å, $b = 25.494(3)$ Å, $c = 10.2372(12)$ Å, $\beta = 112.888(2)^\circ$, $V = 2156.8(49)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0467$, $wR_{ref}(F^2) = 0.1296$, $T = 296(2)$ K.

CCDC no.: 1492201

The two main components of the asymmetric unit of the crystal structure are shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C20	0.62954(19)	0.03924(6)	0.17086(17)	0.0263(3)
C21	0.47420(19)	0.04475(6)	0.17915(18)	0.0292(4)
C22	0.3635(2)	0.07996(7)	0.0946(2)	0.0365(4)
H22	0.2649	0.0837	0.1038	0.044*
C23	0.3951(2)	0.11045(7)	−0.0055(2)	0.0376(4)
H23	0.3192	0.1347	−0.0606	0.045*
C24	0.4196(2)	0.00940(7)	0.26943(19)	0.0326(4)
C25	0.7664(2)	−0.01363(7)	0.40364(19)	0.0337(4)
N1	0.6202(2)	0.12192(6)	0.46113(18)	0.0407(4)
N2	0.4403(2)	0.17174(7)	0.4847(2)	0.0482(4)
N3	1.1208(2)	0.27091(7)	0.12953(19)	0.0436(4)
N4	1.2454(3)	0.21945(7)	0.0464(2)	0.0641(6)
N5	1.1583(2)	0.18932(7)	0.1001(2)	0.0621(6)
N6	1.2228(2)	0.26830(7)	0.0636(2)	0.0503(4)
O1	0.44522(17)	−0.03725(5)	0.27658(15)	0.0430(3)
O2	0.33379(16)	0.03381(5)	0.32937(15)	0.0447(3)
O3	0.81588(19)	−0.05878(5)	0.43785(16)	0.0516(4)
O4	0.72694(15)	0.01845(5)	0.48173(13)	0.0363(3)
O5	0.48534(19)	0.17133(6)	−0.19473(16)	0.0547(4)
O6	0.72044(16)	0.13194(5)	−0.13537(15)	0.0431(3)
O7	0.94400(17)	0.08775(6)	−0.10082(16)	0.0518(4)
O8	0.0431(2)	0.36853(6)	0.1834(2)	0.0587(5)
H7	0.675(3)	0.0905(9)	0.469(2)	0.059(7)*
H3	1.097(3)	0.3038(10)	0.153(3)	0.064(7)*
H8	0.352(3)	0.1853(10)	0.507(3)	0.083(8)*
H12	0.100(4)	0.3920(13)	0.150(4)	0.111(11)*
H13	0.017(3)	0.3791(11)	0.250(3)	0.084(9)*
H11	0.313(3)	0.0106(9)	0.391(3)	0.094(10)*

Source of material

The ethanol solution (5 mL) of 1-(1*H*-imidazol-4-yl)-4-(4*H*-tetrazol-5-yl)benzene (L, 0.10 mmol, 0.021 g) was slowly added to an aqueous solution (25 mL) of 1,4,5,8-naphthalenetetracarboxylic dianhydride (A, 0.10 mmol, 0.026 g). The mixture was stirred for half an hour at 353 K. The solution was filtered, and the filtrate was kept at the room temperature. After two weeks later, colorless crystals were obtained with a yield of 68%. Analysis calculated (%): C, 55.82; H, 3.12; N, 16.27. Found (%): C, 55.69; H, 3.35; N, 16.11.

Experimental details

H atoms bonded to C atoms were placed geometrically and treated as riding except H7, H8, H11, H12, H13 and H3.

Discussion

Cocrystals represent an interesting class of compounds because they are easily accessible, and offer great diversity in terms of composition and properties [1, 2]. Particularly, cocrystals have shown their use, especially in the context of pharmaceuticals because they offer a convenient way to alter the physical properties of a drug without affecting its

therapeutic effects [3]. The polyazaheteroaromatic ligands can exist as anionic ligands due to the deprotonation of N–H groups [4]. For example, nitrogen-rich imidazole ligands, are effective as neutral molecules, and more importantly are likely to act as imidazolate anions to build imidazolate frameworks [5–7]. The nitrogen atoms of nitrogen-rich molecules can serve as weak bases to accept protons from acids to form acid-base conjugate pair, which might potentially benefit the construction of cocrystals. In this regard, some assemblies of different multi-nitrogen ligands such as 4,4′-bipyridine and its higher analogues such as 1,2-di-4-pyridylethylene/ethane with carboxylic acids are reported in the recent literature [8, 9]. As mentioned above, the nitrogen-rich molecule L can serve as weak base to accept protons from carboxylic acid to form organic acid-base adducts. Single-crystal X-ray investigation revealed that the title compound represents an organic salt, as the H7, H8 and H3 protons were easily located on the 4-imidazolyl and tetrazolyl groups according to the difference Fourier map to offer the HL⁺ cation, while the 1,4,5,8-naphthalenetetracarboxylic dianhydride was partially deprotonated to form AOH[−] anion. As shown in the figure, the protonated HL⁺ forms a crystalline acid-base adduct of the stoichiometry 1:1 with AOH[−].

Acknowledgements: This project is supported by Educational Commission of Anhui Province of China (2014KJ016), Natural Science Foundation of Fuyang Normal College (2015FSKJ02ZD, 2014FSKJ06, FS201402001B) and the Innovation Training Program for the College students (201510371034, 201510371041)

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