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Dikhtiarenko, Alla; Olivos Suarez, Alma I.; Pustovarenko, A.; García-Granda, Santiago; Gascon, Jorge

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Alla Dikhtiarenko*, Alma I. Olivos Suarez, Alexey Pustovarenko, Santiago García-Granda and Jorge Gascon

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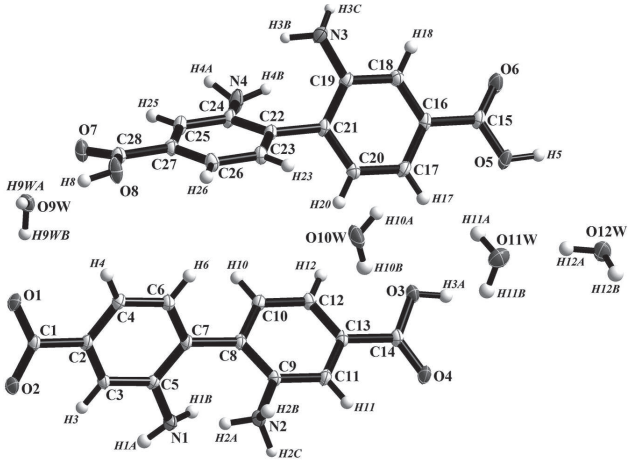

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Abstract

$C_{14}H_{16}N_2O_6$, triclinic, $P\bar{1}$ (no. 2), $a = 10.0254(5)$ Å, $b = 11.2726(6)$ Å, $c = 13.4494(7)$ Å, $\alpha = 111.535(2)°$, $\beta = 92.068(2)°$, $\gamma = 102.644(2)°$, $V = 1368.16(13)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.047$, $wR_{ref}(F^2) = 0.133$, $T = 150$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Alla Dikhtiarenko,** Catalysis Engineering, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, Delft 2628BL, The Netherlands, e-mail: a.dikhtiarenko@tudelft.nl

Alma I. Olivos Suarez, Alexey Pustovarenko and Jorge Gascon: Catalysis Engineering, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, Delft 2628BL, The Netherlands

Santiago García-Granda: Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo – CINN, C/ Julián Clavería, 8, 33006 Oviedo, Spain

Table 1: Data collection and handling.

Crystal:	Yellow, tetrahedral, size 0.10×0.20×0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.18 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Ruby, Gemini, ω scans
$2\theta_{max}$:	61.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	73950, 8404
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6147
$N(param)_{refined}$:	477
Programs:	XABS2 [6], CrysAlis [7], SIR92 [8], SHELX [9], Diamond [10], WinGX [11], enCIFer [12]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.590(2)	0.196(2)	−0.103(2)	0.025(4)
H(1B)	2*i*	0.671(2)	0.235(2)	0.006(2)	0.031(5)
H(2A)	2*i*	0.429(2)	0.097(2)	0.074(1)	0.048(6)
H(2B)	2*i*	0.393(2)	0.067(3)	0.165(2)	0.062(7)
H(2C)	2*i*	0.496(2)	0.003(2)	0.094(2)	0.037(5)
H(3A)	2*i*	0.962(2)	0.307(2)	0.544(2)	0.055(7)
H(3)	2*i*	0.4030	0.2839	−0.1213	0.019
H(4)	2*i*	0.2769	0.5190	0.1431	0.022
H(6)	2*i*	0.4255	0.4714	0.2498	0.022
H(10)	2*i*	0.7131	0.5028	0.2805	0.021
H(11)	2*i*	0.6450	0.0770	0.2676	0.021
H(12)	2*i*	0.8519	0.4582	0.3959	0.020
H(3B)	2*i*	0.748(2)	1.005(2)	0.727(2)	0.034(5)
H(3C)	2*i*	0.842(2)	1.051(2)	0.829(2)	0.034(5)
H(4A)	2*i*	0.859(2)	1.023(2)	0.525(2)	0.048(6)
H(4B)	2*i*	0.897(2)	0.956(2)	0.595(2)	0.040(6)
H(5)	2*i*	1.074(2)	0.559(2)	0.893(2)	0.050(6)
H(8)	2*i*	0.214(3)	0.739(2)	0.264(2)	0.055(7)
H(17)	2*i*	0.8859	0.5307	0.6721	0.022
H(18)	2*i*	0.9468	0.9060	0.8809	0.022
H(20)	2*i*	0.7495	0.5723	0.5533	0.021
H(23)	2*i*	0.5050	0.6379	0.5654	0.022
H(25)	2*i*	0.6460	0.9434	0.4121	0.024
H(26)	2*i*	0.3536	0.6551	0.4413	0.023
H(9WA)	2*i*	0.030(3)	0.700(2)	0.157(2)	0.045(6)
H(9WB)	2*i*	0.136(2)	0.660(2)	0.099(2)	0.050(7)
H(10A)	2*i*	0.096(3)	0.306(3)	0.687(2)	0.056(7)
H(10B)	2*i*	0.101(3)	0.199(3)	0.584(2)	0.080(9)
H(11A)	2*i*	0.158(3)	0.166(3)	0.805(2)	0.074(8)
H(11B)	2*i*	0.144(3)	0.023(3)	0.732(2)	0.074(8)
H(12A)	2*i*	0.231(3)	0.057(3)	0.910(2)	0.067(8)
H(12B)	2*i*	0.215(3)	−0.059(3)	0.950(2)	0.078(9)

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.2193(1)	0.4262(1)	−0.0703(1)	0.0149(6)	0.0169(6)	0.0217(6)	0.0029(5)	−0.0032(5)	0.0101(5)
C(2)	2*i*	0.3226(1)	0.4029(1)	−0.0002(1)	0.0138(6)	0.0151(6)	0.0201(6)	0.0029(4)	−0.0023(5)	0.0093(5)
C(3)	2*i*	0.4079(1)	0.3212(1)	−0.0467(1)	0.0158(6)	0.0164(6)	0.0153(6)	0.0029(5)	−0.0023(5)	0.0075(5)
C(4)	2*i*	0.3311(1)	0.4615(1)	0.1116(1)	0.0189(6)	0.0197(6)	0.0207(6)	0.0099(5)	0.0011(5)	0.0088(5)
C(5)	2*i*	0.5007(1)	0.2943(1)	0.0171(1)	0.0133(6)	0.0144(6)	0.0190(6)	0.0040(4)	0.0004(5)	0.0078(5)
C(6)	2*i*	0.4208(1)	0.4332(1)	0.1752(1)	0.0208(6)	0.0212(6)	0.0162(6)	0.0090(5)	0.0003(5)	0.0080(5)
C(7)	2*i*	0.5043(1)	0.3484(1)	0.1298(1)	0.0140(6)	0.0168(6)	0.0187(6)	0.0044(5)	−0.0014(5)	0.0092(5)
C(8)	2*i*	0.5947(1)	0.3172(1)	0.2022(1)	0.0154(6)	0.0189(6)	0.0150(6)	0.0077(5)	0.0015(5)	0.0085(5)
C(9)	2*i*	0.5761(1)	0.1902(1)	0.2014(1)	0.0153(6)	0.0170(6)	0.0163(6)	0.0053(5)	−0.0008(5)	0.0066(5)
C(10)	2*i*	0.6993(1)	0.4170(1)	0.2772(1)	0.0177(6)	0.0173(6)	0.0194(6)	0.0054(5)	0.0011(5)	0.0099(5)
C(11)	2*i*	0.6589(1)	0.1625(1)	0.2702(1)	0.0183(6)	0.0171(6)	0.0201(6)	0.0062(5)	−0.0006(5)	0.0099(5)
C(12)	2*i*	0.7827(1)	0.3906(1)	0.3467(1)	0.0145(6)	0.0189(6)	0.0170(6)	0.0038(5)	0.0003(5)	0.0080(5)
C(13)	2*i*	0.7629(1)	0.2628(1)	0.3430(1)	0.0158(6)	0.0199(6)	0.0158(6)	0.0070(5)	0.0014(5)	0.0093(5)
C(14)	2*i*	0.8490(1)	0.2311(1)	0.4178(1)	0.0149(6)	0.0201(6)	0.0178(6)	0.0038(5)	−0.0012(5)	0.0095(5)
N(1)	2*i*	0.5840(1)	0.2086(1)	−0.0317(1)	0.0163(5)	0.0205(5)	0.0175(5)	0.0079(4)	0.0004(4)	0.0074(4)
N(2)	2*i*	0.4649(1)	0.0831(1)	0.1298(1)	0.0209(6)	0.0189(6)	0.0195(6)	0.0060(5)	−0.0025(5)	0.0069(5)
O(1)	2*i*	0.1756(1)	0.5284(1)	−0.03006(8)	0.0232(5)	0.0212(5)	0.0246(5)	0.0116(4)	−0.0032(4)	0.0096(4)
O(2)	2*i*	0.1790(1)	0.3419(1)	−0.16484(8)	0.0278(6)	0.0214(5)	0.0226(5)	0.0073(4)	−0.0110(4)	0.0064(4)
O(3)	2*i*	0.9150(1)	0.3343(1)	0.50236(8)	0.0232(5)	0.0220(5)	0.0185(5)	0.0052(4)	−0.0055(4)	0.0083(4)
O(4)	2*i*	0.8550(1)	0.1185(1)	0.40230(9)	0.0317(6)	0.0203(5)	0.0262(5)	0.0079(4)	−0.0085(4)	0.0106(4)
C(15)	2*i*	1.0277(1)	0.6921(1)	0.8622(1)	0.0151(6)	0.0208(6)	0.0230(6)	0.0057(5)	0.0001(5)	0.0123(5)
C(16)	2*i*	0.9326(1)	0.7156(1)	0.7874(1)	0.0134(6)	0.0203(6)	0.0212(6)	0.0050(5)	0.0007(5)	0.0127(5)
C(17)	2*i*	0.8712(1)	0.6143(1)	0.6897(1)	0.0172(6)	0.0173(6)	0.0227(6)	0.0073(5)	0.0010(5)	0.0097(5)
C(18)	2*i*	0.9061(1)	0.8389(1)	0.8153(1)	0.0175(6)	0.0178(6)	0.0195(6)	0.0039(5)	−0.0026(5)	0.0074(5)
C(19)	2*i*	0.8187(1)	0.8627(1)	0.7458(1)	0.0152(6)	0.0165(6)	0.0214(6)	0.0052(5)	0.0003(5)	0.0089(5)
C(20)	2*i*	0.7883(1)	0.6393(1)	0.6194(1)	0.0178(6)	0.0183(6)	0.0175(6)	0.0052(5)	−0.0006(5)	0.0074(5)
C(21)	2*i*	0.7610(1)	0.7631(1)	0.6451(1)	0.0126(6)	0.0184(6)	0.0199(6)	0.0043(5)	0.0002(5)	0.0112(5)
C(22)	2*i*	0.6671(1)	0.7813(1)	0.5667(1)	0.0158(6)	0.0179(6)	0.0174(6)	0.0054(5)	0.0002(5)	0.0087(5)
C(23)	2*i*	0.5334(1)	0.7000(1)	0.5353(1)	0.0173(6)	0.0206(6)	0.0187(6)	0.0033(5)	0.0007(5)	0.0115(5)
C(24)	2*i*	0.7107(1)	0.8727(1)	0.5181(1)	0.0141(6)	0.0206(6)	0.0233(7)	0.0042(5)	−0.0006(5)	0.0125(5)
C(25)	2*i*	0.6184(1)	0.8822(1)	0.4432(1)	0.0177(6)	0.0227(7)	0.0238(7)	0.0050(5)	0.0006(5)	0.0148(5)
C(26)	2*i*	0.4425(1)	0.7095(1)	0.4606(1)	0.0148(6)	0.0224(6)	0.0194(6)	0.0030(5)	−0.0009(5)	0.0094(5)
C(27)	2*i*	0.4855(1)	0.8014(1)	0.4144(1)	0.0171(6)	0.0209(6)	0.0174(6)	0.0072(5)	0.0007(5)	0.0084(5)
C(28)	2*i*	0.3918(1)	0.8121(1)	0.3318(1)	0.0190(6)	0.0219(6)	0.0183(6)	0.0068(5)	−0.0005(5)	0.0078(5)
N(3)	2*i*	0.7786(1)	0.9830(1)	0.7817(1)	0.0254(6)	0.0167(6)	0.0265(6)	0.0075(5)	−0.0034(5)	0.0083(5)
N(4)	2*i*	0.8477(1)	0.9447(1)	0.5355(1)	0.0167(6)	0.0316(7)	0.0413(8)	−0.0015(5)	−0.0063(5)	0.0262(6)
O(5)	2*i*	1.0122(1)	0.5671(1)	0.84319(9)	0.0216(5)	0.0209(5)	0.0305(6)	0.0058(4)	−0.0056(4)	0.0146(4)
O(6)	2*i*	1.1121(1)	0.7807(1)	0.93305(9)	0.0271(6)	0.0242(5)	0.0327(6)	0.0030(4)	−0.0117(4)	0.0137(5)
O(7)	2*i*	0.4297(1)	0.8765(1)	0.27761(9)	0.0269(6)	0.0334(6)	0.0272(6)	0.0043(5)	−0.0048(4)	0.0192(5)
O(8)	2*i*	0.2642(1)	0.7431(1)	0.32201(9)	0.0173(5)	0.0431(7)	0.0295(6)	0.0023(5)	−0.0064(4)	0.0221(5)
O(9W)	2*i*	0.1158(1)	0.7216(1)	0.15266(9)	0.0208(5)	0.0237(5)	0.0226(5)	0.0036(4)	−0.0052(4)	0.0074(4)
O(10W)	2*i*	0.0556(1)	0.2622(2)	0.6247(1)	0.0436(8)	0.0531(8)	0.0213(6)	0.0257(7)	−0.0073(5)	0.0108(6)
O(11W)	2*i*	0.1301(2)	0.0794(1)	0.8041(1)	0.0516(8)	0.0234(6)	0.0401(7)	0.0066(6)	−0.0029(6)	0.0117(5)
O(12W)	2*i*	0.2773(1)	0.0250(1)	0.9551(1)	0.0352(6)	0.0238(6)	0.0328(6)	−0.0002(5)	−0.0120(5)	0.0109(5)

Source of material

2,2′-Dinitrophenyl-4,4′-dicarboxylic acid dimethyl ester was reduced in an ethanolic solution with 5.8 g of $SnCl_2 \cdot H_2O$ and 3 mL of concentrated HCl. After partial evaporation of the solvent, the 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid dimethyl ester was recrystallized from hexane. The final product was obtained after deprotection of the ester with KOH in THF. Yielding (56%) a light-yellow solid. Crystals for X-ray diffraction measurements were grown in TMOS gel media containing 0.37 mmol of 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid, which previously has been neutralized with LiOH, and under-layered with 0.01M HCl. Yellow rectangular shaped crystals of title compound were formed in the gel phase after two weeks.

Experimental details

Hydrogen atoms belonging to carboxylic, amino- groups and water molecules were taken from a ΔF map. All aromatic

and methyl hydrogen atoms were placed in calculated position and then refined with riding model with C—H lengths of 0.93 Å and 0.96 Å ($U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl), respectively.

Discussion

In recent years, research on coordination polymers and metal-organic frameworks has made considerable progress. These microporous crystalline materials exhibit intriguing properties, such as molecular adsorption, magnetism and luminescence [1, 2]. Non-covalent intermolecular interactions, mainly hydrogen bonding and aromatic interactions of aromatic carboxylates play a key role in the crystal packing of such coordination polymers [3, 4]. Although carboxylic linkers are most commonly used to build up metal-organic frameworks [5], the crystal structures of these carboxylic acids are rarely reported. Recently, we crystallize the title compound using TMOS gel media.

The asymmetric unit of the title compound (Figure) contains two 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid and four water molecules. One of the two independent acid molecules is found to be in its zwitterionic form (COO^-/NH_3^+) whereas the other is neutral. Due to steric hindrance, in both carboxylic acid molecules, the planes of the aromatic rings in the biphenyl moiety are twisted with respect to each other with a dihedral angle of 63.4° and 60.1° respectively. Notably, the larger angle of repulsion is attributed to the protonation of the amino-group ($-NH_3^+$) in one of the carboxylic acid molecules. The *cis*-conformation of 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid molecules is established by the weak N2–H2a·N1 and N3–H3b·N4 intramolecular contact with the distance of 3.138(2) Å and 3.299(2) Å. Herein, the planes of all the carboxylic groups are slightly deviated from the planes of the neighbouring aromatic rings and show a dihedral angle of 9.7°, 20.3°, 17.8° and 23.6° for O8–C28–O7, O5–C15–O6, O3–C14–O4 and O1–C1–O2 groups, respectively. The C=O bond lengths of the carboxylic groups C14–O4, C15–O6 and C28–O7 are 1.2236(17) Å, 1.2228(17) Å and 1.2216(17) Å, respectively. The bond lengths of 1.3123(16) Å, 1.3085(17) Å, 1.3170(18) Å for C14–O3, C15–O5 and C28–O8 are as expected. In the O1–C1–O2 carboxylic group the O1–C1 and O2–C1 bond length are nearly equal (1.261 Å and 1.263 Å, respectively), indicating that the double bond in the O1–C1–O2 carboxylic group is delocalized, as a result of deprotonation.

In the crystal, two 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid and four water molecules are linked by intermolecular O–H···N, O–H···O and N–H···N hydrogen bonds. Two co-planar acid molecules are linked *via* O5–H5···O1 to form a dimer moiety that extends through multiple hydrogen bonds involving the carboxylate, the amino groups and water molecules into a 3D hydrogen bonded framework.

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