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The crystal structure of 2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine – dimethylformamide (1/1), C₃₃H₂₈N₁₀O

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.20 × 0.10 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	0.70 mm ⁻¹
Diffraction, scan mode:	Xcalibur, Sapphire3, ω
$\theta_{\max}$, completeness:	62.6°, 97%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	14896, 8933, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6705
$N(\text{param})_{\text{refined}}$:	797
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.57172(17)	0.65629(15)	0.12856(14)	0.0652(5)
O2	−0.13790(13)	0.45860(15)	0.39976(14)	0.0618(5)
N19	0.42517(18)	0.49117(17)	0.08459(16)	0.0574(5)
N20	0.03734(14)	0.56812(14)	0.42334(13)	0.0408(4)
N1	0.18539(12)	0.81656(12)	0.28446(10)	0.0250(3)
N2	0.13234(12)	0.75775(12)	0.11714(10)	0.0264(3)
N3	0.29172(12)	0.92712(12)	0.22555(10)	0.0251(3)
N4	0.33311(12)	0.90493(12)	−0.17205(10)	0.0262(3)
N5	0.41895(13)	0.98654(13)	−0.24828(11)	0.0332(4)
N6	0.58439(12)	1.22399(12)	0.67060(10)	0.0266(3)
N7	0.67483(13)	1.30260(13)	0.82606(11)	0.0343(4)
N8	−0.27986(12)	0.38495(12)	0.12348(10)	0.0254(3)
N9	−0.44086(13)	0.23301(13)	0.04350(11)	0.0319(4)
N10	0.66604(12)	0.79338(12)	0.76520(11)	0.0281(3)
N11	0.73057(12)	0.84086(12)	0.65195(11)	0.0264(3)
N12	0.84019(12)	0.94697(12)	0.81649(10)	0.0258(3)
N13	0.26859(12)	0.42451(12)	0.36708(11)	0.0284(3)
N14	0.11009(14)	0.27015(14)	0.28639(12)	0.0394(4)
N15	1.13073(12)	1.22249(12)	0.64105(11)	0.0279(3)
N16	1.19590(14)	1.31998(14)	0.56949(12)	0.0373(4)
N17	0.81651(12)	0.98023(12)	1.22184(11)	0.0269(3)
N18	0.88457(14)	1.07598(15)	1.38159(12)	0.0394(4)
C61	0.4852(3)	0.4547(2)	0.1257(2)	0.0711(8)
H61A	0.459711	0.441877	0.175650	0.107*
H61B	0.561418	0.511108	0.154014	0.107*
H61C	0.474715	0.386431	0.075093	0.107*
C62	0.3122(2)	0.4139(2)	0.0313(2)	0.0683(7)

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Abstract

C₃₃H₂₈N₁₀O, triclinic, $P\bar{1}$ (no. 2), $a = 14.7148(9)$ Å, $b = 15.5185(10)$ Å, $c = 16.1128(9)$ Å, $\alpha = 113.219(6)^\circ$, $\beta = 96.735(5)^\circ$, $\gamma = 115.259(6)^\circ$, $V = 2872.0(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0426$, $wR_{\text{ref}}(F^2) = 0.1108$, $T = 150(2)$ K.

CCDC no.: 1918542

The molecular structure is shown in the figure (The second crystallographic independent title molecule as well as the two DMF solvent molecules – also present in the asymmetric unit – are not shown for clarity.). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H62A	0.302464	0.351476	−0.026111	0.102*
H62B	0.279984	0.449950	0.012106	0.102*
H62C	0.277469	0.388072	0.071943	0.102*
C63	0.4753(2)	0.5884(2)	0.08997(19)	0.0577(6)
H63	0.432399	0.607476	0.061075	0.069*
C64	0.0399(3)	0.4805(2)	0.3471(2)	0.0679(7)
H64A	−0.028026	0.411503	0.322208	0.102*
H64B	0.098797	0.473589	0.372250	0.102*
H64C	0.050489	0.497224	0.295072	0.102*
C65	0.1345(2)	0.6728(2)	0.4774(2)	0.0610(7)
H65A	0.188434	0.666155	0.511739	0.092*
H65B	0.120824	0.725479	0.523746	0.092*
H65C	0.160634	0.698506	0.433520	0.092*
C66	−0.0528(2)	0.5488(2)	0.44358(18)	0.0500(6)
H66	−0.051626	0.607718	0.494609	0.060*
C1	0.27136(14)	0.90635(14)	0.29663(12)	0.0229(4)
C2	0.35099(14)	0.98837(14)	0.39442(12)	0.0238(4)
C3	0.34123(15)	0.97373(15)	0.47335(13)	0.0284(4)
H3	0.280948	0.909822	0.464818	0.034*
C4	0.41736(15)	1.05017(15)	0.56398(13)	0.0281(4)
H4	0.409874	1.038029	0.616795	0.034*
C5	0.50493(14)	1.14489(14)	0.57752(12)	0.0242(4)
C6	0.51487(15)	1.16109(15)	0.49943(13)	0.0291(4)
H6	0.574145	1.225936	0.508279	0.035*
C7	0.43923(15)	1.08363(15)	0.40921(13)	0.0277(4)
H7	0.447392	1.095363	0.356287	0.033*
C8	0.59155(16)	1.21552(16)	0.75199(13)	0.0311(4)
H8	0.541839	1.153561	0.754743	0.037*
C9	0.72516(17)	1.37061(16)	0.79081(14)	0.0367(5)
H9	0.788826	1.440580	0.827769	0.044*
C10	0.67181(17)	1.32443(16)	0.69669(14)	0.0368(5)
H10	0.690638	1.354986	0.656162	0.044*
C11	0.22200(14)	0.84917(14)	0.13733(12)	0.0232(4)
C12	0.24718(14)	0.86438(14)	0.05610(12)	0.0240(4)
C13	0.34150(14)	0.95655(15)	0.07384(13)	0.0261(4)
H13	0.387358	1.010510	0.138280	0.031*
C14	0.36926(14)	0.97060(14)	−0.00058(13)	0.0259(4)
H14	0.433710	1.033906	0.012618	0.031*
C15	0.30256(15)	0.89173(15)	−0.09521(13)	0.0251(4)
C16	0.20743(15)	0.80054(15)	−0.11398(13)	0.0302(4)
H16	0.161036	0.747431	−0.178432	0.036*
C17	0.18021(15)	0.78698(15)	−0.03900(13)	0.0299(4)
H17	0.115131	0.724228	−0.052326	0.036*
C18	0.40805(15)	1.00043(15)	−0.16532(13)	0.0279(4)
H18	0.447515	1.068774	−0.107219	0.033*
C19	0.34822(17)	0.87675(17)	−0.31157(14)	0.0373(5)
H19	0.338119	0.841866	−0.378168	0.045*
C20	0.29509(17)	0.82496(16)	−0.26724(13)	0.0353(5)
H20	0.242573	0.749412	−0.295449	0.042*
C21	0.11747(14)	0.74657(14)	0.19359(12)	0.0235(4)
C22	0.01673(14)	0.64977(14)	0.17524(13)	0.0252(4)
C23	−0.05067(16)	0.56667(16)	0.08205(13)	0.0315(4)
H23	−0.030142	0.570986	0.029420	0.038*
C24	−0.14665(16)	0.47810(16)	0.06423(14)	0.0335(4)
H24	−0.190309	0.420869	0.000127	0.040*
C25	−0.17904(14)	0.47313(14)	0.14062(13)	0.0251(4)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C26	−0.11287(15)	0.55588(15)	0.23432(13)	0.0281(4)
H26	−0.134818	0.552991	0.286790	0.034*
C27	−0.01544(15)	0.64213(15)	0.25122(13)	0.0281(4)
H27	0.030257	0.696988	0.315501	0.034*
C28	−0.35669(15)	0.30204(15)	0.03566(13)	0.0280(4)
H28	−0.349511	0.295548	−0.024016	0.034*
C29	−0.41702(16)	0.27148(16)	0.14119(14)	0.0326(4)
H29	−0.463154	0.237423	0.169412	0.039*
C30	−0.31959(16)	0.36382(16)	0.19136(14)	0.0319(4)
H30	−0.285396	0.405616	0.259218	0.038*
C31	0.76109(14)	0.87840(14)	0.83269(13)	0.0247(4)
C32	0.77861(14)	0.90034(14)	0.93283(13)	0.0254(4)
C33	0.69888(15)	0.83522(15)	0.95673(13)	0.0289(4)
H33	0.634737	0.772494	0.907146	0.035*
C34	0.71158(15)	0.86033(15)	1.05103(13)	0.0294(4)
H34	0.656193	0.815256	1.065907	0.035*
C35	0.80511(14)	0.95132(15)	1.12436(13)	0.0258(4)
C36	0.88713(15)	1.01502(16)	1.10170(13)	0.0308(4)
H36	0.952543	1.075592	1.151164	0.037*
C37	0.87317(15)	0.98997(16)	1.00721(14)	0.0301(4)
H37	0.929040	1.034619	0.992437	0.036*
C38	0.89546(16)	1.07536(17)	1.30185(14)	0.0348(4)
H38	0.951608	1.134095	1.299775	0.042*
C39	0.79441(16)	0.97643(18)	1.35205(14)	0.0356(5)
H39	0.766215	0.952986	1.394365	0.043*
C40	0.75129(16)	0.91650(17)	1.25532(14)	0.0321(4)
H40	0.689129	0.845393	1.217886	0.038*
C41	0.82059(14)	0.92540(14)	0.72493(12)	0.0244(4)
C42	0.90241(14)	1.00157(15)	0.70320(13)	0.0254(4)
C43	0.88365(15)	0.98521(15)	0.60973(13)	0.0275(4)
H43	0.819010	0.923818	0.559790	0.033*
C44	0.95871(15)	1.05796(15)	0.58959(13)	0.0275(4)
H44	0.945359	1.046761	0.525979	0.033*
C45	1.05343(15)	1.14723(15)	0.66203(13)	0.0262(4)
C46	1.07278(15)	1.16514(15)	0.75557(13)	0.0285(4)
H46	1.137264	1.226935	0.805421	0.034*
C47	0.99723(15)	1.09212(15)	0.77548(13)	0.0275(4)
H47	1.010371	1.104056	0.839328	0.033*
C48	1.10997(16)	1.24122(15)	0.56664(13)	0.0311(4)
H48	1.041565	1.201866	0.518799	0.037*
C49	1.27594(16)	1.35337(17)	0.64857(14)	0.0362(5)
H49	1.348275	1.409706	0.668960	0.043*
C50	1.23790(15)	1.29520(16)	0.69359(14)	0.0341(4)
H50	1.277184	1.303011	0.749898	0.041*
C51	0.65583(15)	0.77769(14)	0.67564(13)	0.0257(4)
C52	0.55456(15)	0.68584(15)	0.59667(13)	0.0268(4)
C53	0.45988(16)	0.63714(16)	0.61373(13)	0.0328(4)
H53	0.460454	0.661976	0.678036	0.039*
C54	0.36510(16)	0.55334(16)	0.53880(14)	0.0340(4)
H54	0.300662	0.522983	0.551463	0.041*
C55	0.36481(15)	0.51389(14)	0.44491(13)	0.0275(4)
C56	0.45833(16)	0.56092(16)	0.42677(13)	0.0323(4)
H56	0.458199	0.533973	0.362574	0.039*
C57	0.55182(15)	0.64698(16)	0.50191(14)	0.0322(4)
H57	0.615164	0.680103	0.488685	0.039*
C58	0.18675(16)	0.34059(15)	0.36996(14)	0.0330(4)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
H58	0.185701	0.334198	0.426144	0.040*
C59	0.14318(17)	0.30950(17)	0.22578(14)	0.0392(5)
H59	0.103465	0.275424	0.159644	0.047*
C60	0.24011(17)	0.40346(16)	0.27322(14)	0.0351(5)
H60	0.280265	0.446127	0.247358	0.042*

Source of material

Procedures for preparation of 2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine (TIPT) adapted from the reported paper [11]. The characterization of TIPT was performed by comparison of its 1H NMR and IR spectrum with those reported previously. 1H -NMR (300 MHz, DMSO- d_6): δ [ppm] 8.80 (d, $J = 8.7$ Hz, 6H), 8.46 (s, 3H), 7.96–7.87 (m, 9H), 7.18 (s, 3H); IR (cm^{-1}): 1604(s), 1522(vs), 1487(s), 1400(w), 1303(s), 1261(m), 1108(w), 1057(vs), 962(m), 904(w), 825(s), 730(m), 695(m), 638(w), 588(m).

The crystal of *N,N*-dimethylformamide solvate 2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine was synthesized by the following procedure. 3 mL of acetonitrile was layered onto a solution of TIPT (10 mg) in 3 mL *N,N*-dimethylformamide in a test tube. Colorless crystals were formed after several days. Yield: 60%.

Experimental details

Single-crystal X-ray diffraction data for the title structure was collected on Oxford Diffraction Xcalibur CCD diffractometer [1]. The structure was solved with the ShelXT [2] structure solution program and refined with XL [3] refinement package. The positions of the hydrogen atoms were generated geometrically. The figure was drawn by Diamond 4.0 [4].

Comment

Triangle rigid ligand play an important role in the field for construction of metal-organic frameworks (MOFs). As a triangle rigid ligand, 1,3,5-tris(pimidazol-ylphenyl)-benzene (TIPB) was used for construction of more than 20 reported structures [5–10]. However, as a similar triangle rigid ligand, there are only 3 structures related to 2,4,6-tris[4-(1*H*-imidazol-1-yl)phenyl]-1,3,5-triazine (TIPT) reported [11, 12].

The title compound crystallized in space group $P\bar{1}$ and an asymmetric unit contains two TIPT and two *N,N*-dimethylformamide molecules. The bond lengths and angles within these moieties are in the expected ranges. Viewing imidazole ring closer for C–N bond, the distance of C8–N6, C18–N4, C28–N8, C38–N17, C48–N15, C58–N16 is 1.365(2) Å, 1.369(2) Å, 1.372(2) Å, 1.369(3) Å, 1.371(2) Å and 1.368(2) Å, respectively. For C=N bond, the distance of C8–N7, C18–N5, C28–N9, C38–N18, C48–N16, C58–N14 is 1.313(3) Å,

1.308(2) Å, 1.307(2) Å, 1.310(3) Å, 1.311(2) Å and 1.308(2) Å, respectively. The angle of is N6–C8–N7, N4–C18–N5, N8–C28–N9, N17–C38–N18, N15–C48–N16, N13–C58–N14 is 112.45(16)°, 112.09(16)°, 112.30(15)°, 112.18(17)°, 111.83(17)°, 112.19(17)°, respectively.

In the structure of the title compound, there are many different $\pi \cdots \pi$ interactions. First, we define that 5-membered ring N4–C18–N5–C19–C20 is named Ring 2(R1), 5-membered ring N6–C8–N7–C9–C10 is named Ring 2(R2), 5-membered ring N8–C28–N9–C29–C30 is named Ring 3(R3), 6-membered ring N1–C1–N3–C11–N2–C21 is named Ring 4(R4), 6-membered ring C2–C3–C4–C5–C6–C7 is named Ring 5(R5), 6-membered ring C12–C13–C14–C15–C16–C17 is named Ring 6(R6), 5-membered ring N13–C58–N14–C59–C60 is named Ring 7(R7), 5-membered ring N17–C38–N18–C39–C40 is named Ring 8(R8), 6-membered ring N10–C31–N12–C41–N11–C51 is named Ring 9(R9), 6-membered ring C32–C33–C34–C35–C36–C37 is named Ring 10(R10), 6-membered ring C42–C43–C44–C45–C46–C47 is named Ring 11(R11). The distance of center-to-center between two rings for CR1–CR8, CR2–CR4, CR3–CR6, CR4–CR11, CR5–CR5, CR6–CR10, CR7–CR9 and CR8–CR11 is 3.6798(2) Å, 3.5902(2) Å, 3.5678(2) Å, 3.8136(2) Å, 3.6402(2) Å, 3.6263(2) Å, 3.5978(2) Å and 3.5750(2) Å, respectively. π - π interactions connect the structure to a three dimensional framework. Void space between TIPT molecules in the structure are occupied by *N,N*-dimethylformamide solvent molecules.

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References

1. Oxford Diffraction: CrysAlis^{PRO}. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England (2006).
2. Sheldrick, G. M.: SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.0. Crystal Impact, Bonn, Germany (2015).
5. Chen, Q.; Chang, Z.; Song, W.-C.; Song, H.; Song, H.-B.; Hu, T.-L.; Bu, X.-H.: A controllable gate effect in cobalt(II) organic frameworks by reversible structure transformations. *Angew. Chem. Int. Ed.* **52** (2013) 11550–11553.

6. Chen, Q.; Jia, Y.-Y.; Chang, Z.; Wang, T.-T.; Zhou, B.-Y.; Feng, R.; Bu, X.-H.: Pillared metal-organic frameworks based on 6³ layers: structure modulation and sorption properties. *Cryst. Growth Des.* **14** (2014) 5189–5195.
7. Li, Y.; Song, H.; Chen, Q.; Liu, K.; Zhao, F.-Y.; Ruan, W.-J.; Chang, Z.: Two coordination polymers with enhanced ligand-centered luminescence and assembly imparted sensing ability for acetone. *J. Mater. Chem.* **A2** (2014) 9469–9473.
8. Chen, Q.; Feng, R.; Xu, J.; Jia, Y.-Y.; Wang, T.-T.; Chang, Z.; Bu, X.-H.: Kinetic and thermodynamic control of structure transformations in a family of cobalt(II)-organic frameworks. *ACS Appl. Mater. Interfaces* **9** (2017) 35141–35149.
9. Chen, Q.; Ma, Y.-G.; Song, W.-C.; Chang, Z.; Li, J.-R.; Zhang, J.; Sun, H.-W.; Balbuena, P. B.; Bu, X.-H.: Why porous materials have selective adsorptions: a rational aspect from electrodynamics. *Inorg. Chem.* **56** (2017) 2614–2620.
10. Zeng, X.-S.; Xu, H.-L.; Xu, Y.-C.; Li, X.-Q.; Nie, Z.-Y.; Gao, S.-Z.; Xiao, D.-R.: A series of porous interpenetrating metal-organic frameworks based on fluorescent ligands for nitroaromatic explosive detection. *Inorg. Chem. Front.* **5** (2018) 1622–1632.
11. Zheng, S.-R.; Yang, Q.-Y.; Liu, Y.-R.; Zhang, J.-Y.; Tong, Y.-X.; Zhao, C.-Y.; Su, C.-Y.: Assembly of CdI₂-type coordination networks from triangular ligand and octahedral metal center: topological analysis and potential framework porosity. *Chem. Commun.* **44** (2008) 356–358.
12. Zheng, S.-R.; Yin, S.-Y.; Pan, M.; Chen, L.; Du, B.-B.; Hou, Y.-J.; Wu, K.; Zhu, Y.-X.; Jiang, J.-J.: Structural transition between a (4,4)-net and a CdI₂-net in Cd(II) compounds and conversion from a mixture to a pure substance. *Inorg. Chem. Commun.* **55** (2015) 116–119.