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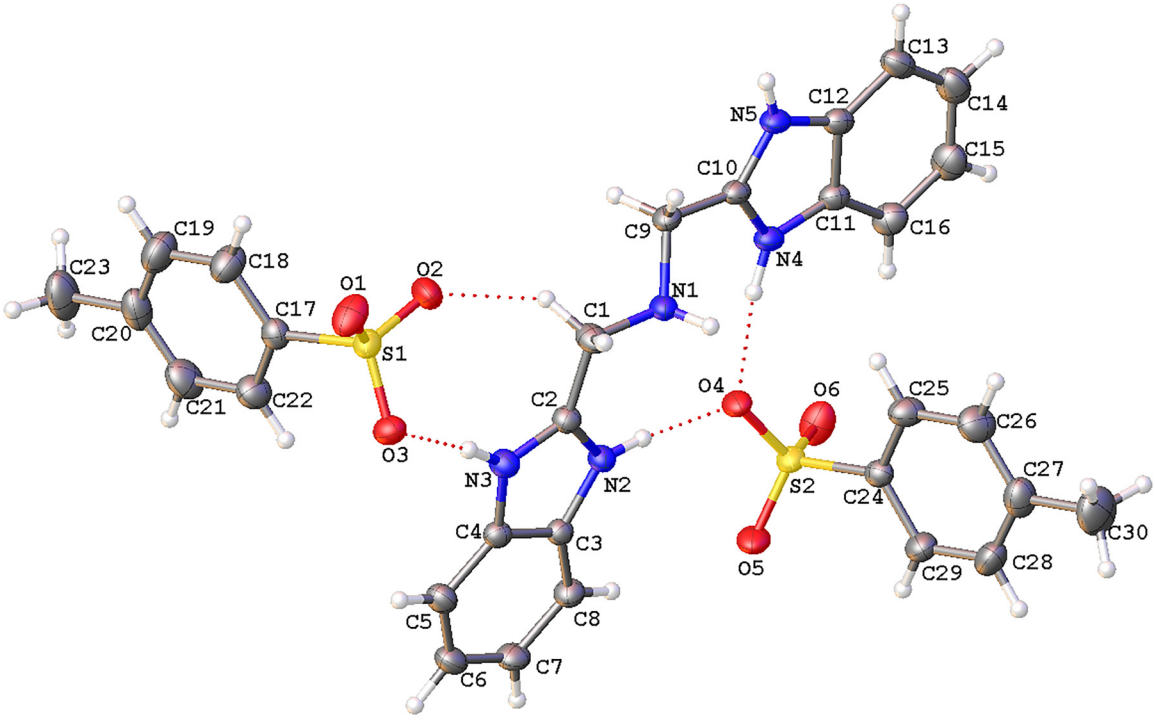
Crystal structure of 2,2′-(iminobis(methylene)) bis(benzimidazolium) bis(*p*-toluenesulfonate), $C_{30}H_{31}N_5O_6S_2$



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Abstract

$C_{30}H_{31}N_5O_6S_2$, Triclinic, $P\bar{1}$ (no. 2), a = 9.8856(3) Å, b = 10.9499(4) Å, c = 14.5715(5) Å, α = 101.939(1)°, β = 92.80(1)°, γ = 106.580(1)°, V = 1469.21(9) Å^3, Z = 2, T = 200 K, $R_{gt}(F)$ = 0.0495, $wR_{ref}(F^2)$ = 0.1538.

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The molecular structure is shown in the figure. 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 1: Data collection and handling.

Crystal:	Colorless block
Size	0.30 × 0.20 × 0.20 mm
Wavelength:	Ga *Kα* radiation (1.34139 Å)
μ:	1.37 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE, φ and ω
θ_{max}, completeness:	72.3°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	49,293, 8,746, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 7,915
$N(param)_{refined}$:	406
Programs:	Bruker,[1] SHELX,[2,3,6] Diamond,[4] Olex2[5]

1 Source of materials

All the reagents and solvents were used as obtained without further purification. Bis((benzimidazol-2-yl)methyl) amine (IDB) was prepared according to a slightly modified method described by Adams et al.[7] The ligand IDB (27.7 mg, 0.1 mmol) and p-toluenesulfonic acid (34.4 g, 0.2 mmol) were thoroughly mixed and dissolved in 10.0 mL methanol solution. The

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.60211 (15)	0.88932 (16)	0.53249 (12)	0.0307 (3)
H1A	0.550479	0.890108	0.589033	0.037*
H1B	0.588154	0.959022	0.502768	0.037*
C2	0.75641 (14)	0.91684 (14)	0.56159 (10)	0.0237 (3)
C3	0.97162 (14)	0.89467 (13)	0.57903 (9)	0.0220 (2)
C4	0.97453 (14)	1.01670 (14)	0.63286 (10)	0.0230 (2)
C5	1.09660 (16)	1.10286 (15)	0.68854 (11)	0.0290 (3)
H5	1.098151	1.186033	0.724957	0.035*
C6	1.21561 (16)	1.05986 (17)	0.68756 (12)	0.0321 (3)
H6	1.301722	1.115395	0.723924	0.038*
C7	1.21218 (15)	0.93633 (17)	0.63419 (12)	0.0314 (3)
H7	1.295973	0.910450	0.636277	0.038*
C8	1.09072 (15)	0.85065 (15)	0.57850 (11)	0.0274 (3)
H8	1.088918	0.767269	0.542321	0.033*
C9	0.39273 (14)	0.70540 (15)	0.47086 (10)	0.0260 (3)
H9B	0.338200	0.758897	0.448656	0.031*
H9A	0.375177	0.702372	0.536784	0.031*
C10	0.34681 (13)	0.57103 (14)	0.40996 (10)	0.0238 (3)
C11	0.35766 (14)	0.38260 (14)	0.32450 (10)	0.0257 (3)
C12	0.21648 (14)	0.38391 (15)	0.31638 (10)	0.0260 (3)
C13	0.10900 (16)	0.28015 (17)	0.25994 (12)	0.0335 (3)
H13	0.013152	0.281011	0.254269	0.040*
C14	0.1498 (2)	0.17572 (17)	0.21260 (13)	0.0392 (4)
H14	0.079766	0.102727	0.173298	0.047*
C15	0.2918 (2)	0.17379 (17)	0.22060 (14)	0.0394 (4)
H15	0.314694	0.099645	0.186837	0.047*
C16	0.39889 (18)	0.27743 (16)	0.27654 (12)	0.0333 (3)
H16	0.494858	0.276857	0.281909	0.040*
N1	0.54421 (12)	0.76341 (13)	0.46645 (9)	0.0260 (2)
H1	0.555 (2)	0.773 (2)	0.4056 (15)	0.031*
N2	0.83250 (12)	0.83517 (12)	0.53554 (8)	0.0230 (2)
H2	0.796 (2)	0.760 (2)	0.4986 (15)	0.028*
N3	0.83836 (12)	1.02692 (12)	0.61950 (9)	0.0249 (2)
H3	0.812 (2)	1.096 (2)	0.6501 (15)	0.030*
N4	0.43484 (12)	0.50080 (12)	0.38439 (9)	0.0245 (2)
H4	0.532 (2)	0.530 (2)	0.3997 (15)	0.029*
N5	0.21481 (12)	0.50303 (13)	0.37166 (9)	0.0260 (2)
H5A	0.141 (2)	0.527 (2)	0.3764 (15)	0.031*
C17	0.66183 (16)	1.19534 (14)	0.87118 (10)	0.0274 (3)
C18	0.5537 (2)	1.1999 (2)	0.92812 (13)	0.0411 (4)
H18	0.470233	1.215630	0.904885	0.049*
C19	0.5682 (2)	1.1814 (2)	1.01915 (14)	0.0479 (5)
H19	0.494262	1.184923	1.057914	0.058*
C20	0.6889 (2)	1.15793 (18)	1.05433 (13)	0.0411 (4)
C21	0.7962 (2)	1.1548 (2)	0.99695 (14)	0.0457 (4)
H21	0.879834	1.139578	1.020396	0.055*
C22	0.78387 (19)	1.17358 (19)	0.90542 (13)	0.0372 (4)
H22	0.858472	1.171440	0.867005	0.045*
C23	0.7022 (3)	1.1355 (2)	1.15307 (15)	0.0565 (6)
H23A	0.774235	1.090980	1.158526	0.085*
H23B	0.610566	1.081177	1.165488	0.085*
H23C	0.730411	1.219975	1.199099	0.085*
O1	0.56683 (15)	1.30587 (14)	0.75218 (9)	0.0413 (3)
O2	0.54799 (12)	1.07599 (13)	0.70167 (9)	0.0396 (3)
O3	0.77714 (11)	1.23848 (11)	0.72020 (8)	0.0309 (2)
S1	0.63572 (3)	1.20569 (4)	0.75266 (2)	0.02644 (11)
C24	0.80725 (14)	0.53929 (13)	0.24491 (10)	0.0244 (3)
C25	0.67968 (16)	0.54733 (18)	0.20599 (12)	0.0342 (3)
H25	0.601686	0.542454	0.242139	0.041*
C26	0.6670 (2)	0.5625 (2)	0.11411 (14)	0.0417 (4)
H26	0.579270	0.567093	0.087679	0.050*
C27	0.7797 (2)	0.57117 (19)	0.05978 (13)	0.0406 (4)
C28	0.9067 (2)	0.56505 (19)	0.10041 (13)	0.0405 (4)
H28	0.985452	0.572643	0.064819	0.049*
C29	0.92167 (17)	0.54806 (17)	0.19196 (12)	0.0334 (3)
H29	1.009072	0.542492	0.218067	0.040*
C30	0.7651 (3)	0.5883 (3)	−0.04041 (16)	0.0623 (6)
H30A	0.859581	0.624009	−0.059089	0.093*
H30B	0.709446	0.648653	−0.043823	0.093*
H30C	0.716696	0.503214	−0.083120	0.093*
O4	0.73325 (10)	0.58172 (11)	0.41444 (8)	0.0284 (2)
O5	0.97546 (11)	0.58327 (14)	0.39779 (9)	0.0385 (3)
O6	0.78284 (16)	0.37789 (12)	0.35497 (9)	0.0409 (3)
S2	0.82679 (3)	0.51735 (3)	0.36129 (2)	0.02405 (10)

resulting clear solution was kept at ambient condition. Colorless block crystals were obtained five days later at the bottom of the vessel. For a better X-ray data collection crystals selected have been immersed into perfluoroalkylether, which was then cooled down to −73 °C during the measurement.

2 Experimental details

H atoms bound to carbon atoms were placed at their geometrically idealized positions and constrained to ride on their parent atoms with C–H = 0.95 Å (aromatic), 0.99 Å (methylene), 0.98 Å (methyl), U_{iso}(H) = 1.2U_{eq} (aromatic and methylene) and 1.5U_{eq} (methyl). Those H atoms bound with N1–N5 atoms were found initially from the difference maps with N–H distances being refined freely, and the U_{iso} values being set 1.2 times of their respective parent atoms.

3 Comment

Bis(2-benzimidazylmethyl)amine (IDB) is a type of multi-benzimidazole ligands which have been often used in the synthesis of various metal-organic complexes used as functional materials.[7] For instance, by employing a tripodal bis(benzimidazole) ligand bis((benzimidazol-2-yl) methyl) amine(IDB) and its derivative as the main ligand, a series of nickel and copper complexes were synthesized which allow a systematic investigation of a biomimetic chemistry.[8] By

using multi- or poly-benzimidazole derivatives, we can improve the properties of a fiber such as reducing flame shrinkage and oxidative resistance.[9] In order to study the flame retardancy of ligands with two benzimidazole, we synthesized a new organic ligand and successfully obtained its p-methylbenzene sulfonate. By introducing a wide variety of anions, we expect to be able to improve the ignition point of the compound as a flame retardant material.

The titled compound was crystallized in the triclinic $P\bar{1}$ space group with one IDB dication and two p-toluenesulfonate anions in its asymmetric unit, forming a 1:2 organic salt. The IDB molecule adopts a nearly planar conformation which is reflected by the torsion angle of –N1–C1–C2–N3– (177.6(1)°), –N1–C9–C10–N5 (–157.3(1)°) and the dihedral angle between two benzimidazole groups (6.1(1)°) which is similar to some analogs.[10–13] The bonds C2–N2 (1.335(1)), C2–N3 (1.333(1)), C10–N4 (1.335(1) and C10–N5 (1.331(1)) are almost equal to each other, indicating the protonation of the benzimidazole nitrogen atoms. What's more, all the nitrogen-bonded hydrogen atoms can be clearly found from the difference maps, which also indicates that the protonation positions are at the benzimidazole nitrogen atoms, instead of the amine N1 atom. Due to the deprotonation of the two p-toluenesulfonic acids, the three S–O bond distances in the two anions are also very close to each other, in a range of 1.445(1)–1.472(1) Å.

In the crystal packing, the ions are linked into a three-dimensional network. In order to simplify the analysis of the crystal packing, it can be introduced in terms of three aspects. Firstly, the IDB cations and p-toluenesulfonate anions are linked together via four N–H···O hydrogen bonds, forming the one-dimensional chain running along the [100] axis. Meanwhile, one $\pi\cdots\pi$ stacking interaction was observed between symmetry-related benzene ring (C3–C8) and imidazole ring (N2/N3/C2/C3/C4) with the centroid-to-centroid distance of 3.511(1) Å. Secondly, these adjacent [100] hydrogen chains are linked by one other $\pi\cdots\pi$ stacking interaction between symmetry-related benzene ring (C11–C16) and imidazole ring (N2/N3/C2/C3/C4) with the centroid-to-centroid distance of 3.523(1) Å, forming a two-dimensional layer structure parallel to the (001) plane. Finally, by analysis using PLATON[14] those neighboring two-dimensional (001) layer structures are linked by weak C–H···π interaction originating from the methyl group (C23) and benzene ring (C4–C8) with the nearest C···C distance being 3.475(1) Å, giving the final three-dimensional network.

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