Crystal structure of bis(2-benzimidazolylmethyl)amino-2-methylbenzimidazolium 3-nitrobenzoate 3-nitrobenzoic acid, $(C_{24}H_{22}N_7)(C_7H_4NO_4)(C_7H_5NO_4)$

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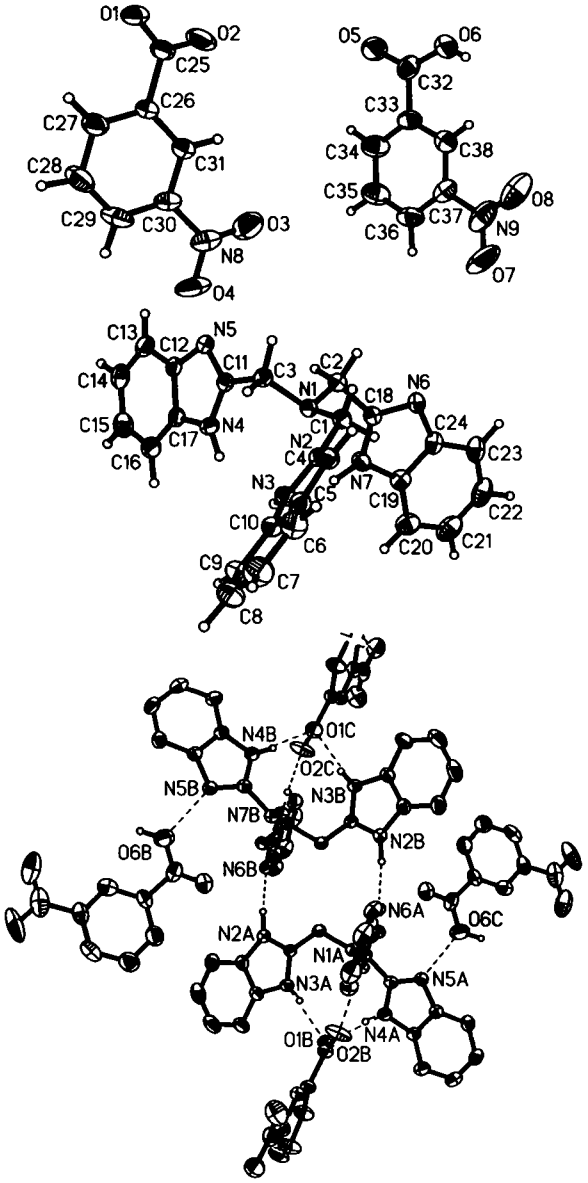

Abstract

$C_{38}H_{31}N_9O_8$, triclinic, $P\bar{1}$ (no. 2), a = 12.268(1) Å, b = 12.491(1) Å, c = 13.348(1) Å, α = 91.230(2)°, β = 100.087(2)°, γ = 114.919(1)°, V = 1816.0 Å^3, Z = 2, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.114, T = 293 K.

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Source of material

The title compound was prepared by reaction of tris(2-benzimidazolylmethyl)amine with 3-nitrobenzoic acid (molar ratio = 1:4) in methanol solution. Single crystals of the title compound suitable for X-ray measurements were obtained by recrystallization from methanol solution at room temperature.

Discussion

The hydrogen-bonded interactions including C–H···O interactions play crucial roles in making supramolecular assemblies. Multicomponent crystals and acid-base complexes have received considerable attention in recent literature for the predictable assembly of supramolecular architectures, host-guest materials and interpenetrated networks. However, so far only a few papers on it formed stable hydrogen-bonded inclusion complexes with aromatic acid have been reported although it possesses both multiple hydrogen bond donor and acceptor sites [1]. Furthermore, the molecules containing imidazole unit are of particular interest since study on their supramolecular properties may shed light on the aggregation nature of proteins.

In the title structure the tris(2-benzimidazolylmethyl)amine moiety adopt a slightly distorted tripod conformation (figure, top), similar to that found in metal complex [2]. Each of the benzimidazole rings is planar within 0.01 Å of deviations and the dihedral angles between them are 47.46(2)° (ring 1 and ring 2), 68.74(3)° (ring 1 and ring 3) and 71.35(2)° (ring 2 and ring 3), respectively (ring 1 includes N2 and N3, ring 2 includes N4 and N5, ring 3 includes N6 and N7). Bond lengths and angles are in expected ranges. The cation is donor to and acceptor from its centrosymmetric cation by N2–H19···N6 hydrogen bond, is donor to the anion O1 and O2 atoms in N3–H20···O1, N4–H21···O1, N7–H22···O2, and is acceptor from the acid molecule in the O6···N5 hydrogen bond. Weaker interactions which involve the cation as donor are: C1–H2···O4 with the anion and C2–H4···O8 with the undissociated acid molecule. The weak C–H···O interactions in the anion and in the undissociated acid molecule are coresponsible for the planar conformation of these constituents (figure, bottom). The molecules are stacked along the c-axis through π-π interactions. The distances for (N4,C11,N5,C12,C17) at x,y,z and (N4,C11,N5,C12,C17) at $1-x,1-y,-z$ are DC = 3.549(3) Å, DP = 3.507(9) Å, SH = 0.54(6) Å; for (C5 → C10) at x,y,z and (C5 → C10) at $2-x,1-y,1-z$ are DC = 3.923(3) Å, DP = 3.44(1) Å, SH = 1.88(2) Å; for (C19 → C24) at x,y,z and (C19 → C24) at $1-x,2-y,1-z$ are DC = 3.654(5) Å, DP = 3.39(2) Å, SH = 1.37(5) Å, where DC is the distances between the ring-centroids, DP is the distances between the planes through the rings and SH is the centroid shift.

Table 1. Data collection and handling.

Crystal:	colorless pillar, size 0.15 × 0.20 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.98 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	53°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10434, 7375
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4002
$N(param)_{refined}$:	621
Programs:	SHELXS-97 [3], SHELXL-97 [4], SHELXTL [5], WinGX [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.604(2)	0.580(2)	0.456(1)	0.046(5)
H(2)	2*i*	0.515(2)	0.446(2)	0.408(1)	0.044(5)
H(3)	2*i*	0.377(2)	0.550(2)	0.364(1)	0.041(5)
H(4)	2*i*	0.392(2)	0.627(2)	0.273(2)	0.061(6)
H(5)	2*i*	0.385(2)	0.425(2)	0.216(1)	0.039(5)
H(6)	2*i*	0.524(2)	0.447(2)	0.206(1)	0.042(5)
H(7)	2*i*	0.870(2)	0.309(2)	0.452(2)	0.066(7)
H(8)	2*i*	1.042(2)	0.370(2)	0.380(2)	0.071(8)
H(9)	2*i*	1.104(2)	0.527(2)	0.284(2)	0.100(9)
H(10)	2*i*	0.980(2)	0.631(2)	0.251(2)	0.082(9)
H(11)	2*i*	0.241(2)	0.578(2)	–0.120(2)	0.060(7)
H(12)	2*i*	0.338(2)	0.734(2)	–0.217(2)	0.063(7)
H(13)	2*i*	0.547(2)	0.857(2)	–0.165(2)	0.072(7)
H(14)	2*i*	0.666(2)	0.826(2)	–0.018(2)	0.076(8)
H(15)	2*i*	0.793(2)	1.037(2)	0.468(2)	0.064(7)
H(16)	2*i*	0.777(2)	1.148(2)	0.604(2)	0.076(8)
H(17)	2*i*	0.619(2)	1.085(2)	0.693(2)	0.080(7)
H(18)	2*i*	0.465(2)	0.895(2)	0.646(2)	0.060(7)
H(19)	2*i*	0.657(2)	0.361(2)	0.453(2)	0.13(1)
H(20)	2*i*	0.775(2)	0.633(2)	0.297(2)	0.051(7)
H(21)	2*i*	0.638(2)	0.679(2)	0.140(2)	0.068(7)
H(22)	2*i*	0.656(2)	0.816(2)	0.357(2)	0.075(8)
H(23)	2*i*	–0.021(2)	–0.143(2)	0.114(2)	0.071(7)
H(24)	2*i*	0.163(2)	0.000(2)	0.094(2)	0.11(1)
H(25)	2*i*	0.271(2)	0.170(2)	0.213(2)	0.086(8)
H(26)	2*i*	–0.005(2)	0.046(2)	0.369(2)	0.061(7)
H(27)	2*i*	0.384(2)	0.943(2)	0.984(2)	0.090(8)
H(28)	2*i*	0.256(3)	0.961(3)	0.834(2)	0.14(1)
H(29)	2*i*	0.049(2)	0.821(2)	0.796(2)	0.10(1)
H(30)	2*i*	0.090(2)	0.675(2)	1.050(2)	0.076(8)
H(31)	2*i*	–0.2069(3)	0.566(4)	0.957(3)	0.22(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*i*	–0.1995(1)	–0.2515(1)	0.2020(1)	0.0490(9)	0.0442(9)	0.075(1)	0.0039(8)	0.0067(8)	0.0096(8)
O(2)	2*i*	–0.2131(2)	–0.1170(2)	0.3033(2)	0.066(1)	0.085(1)	0.129(2)	–0.002(1)	0.059(1)	–0.008(1)
O(3)	2*i*	0.1590(2)	0.2364(2)	0.4456(2)	0.091(2)	0.089(2)	0.107(2)	0.029(1)	0.002(1)	–0.027(1)
O(4)	2*i*	0.3128(2)	0.2927(2)	0.3726(2)	0.061(1)	0.065(1)	0.114(2)	–0.013(1)	–0.017(1)	0.017(1)
O(5)	2*i*	–0.1473(2)	0.6557(2)	0.8117(2)	0.066(1)	0.110(2)	0.088(1)	0.034(1)	0.005(1)	0.023(1)
O(6)	2*i*	–0.1244(2)	0.6041(2)	0.9695(2)	0.073(1)	0.120(2)	0.080(1)	0.006(1)	0.018(1)	0.030(1)
O(7)	2*i*	0.4353(2)	0.8685(3)	1.1386(2)	0.071(2)	0.256(3)	0.114(2)	0.083(2)	–0.034(1)	–0.081(2)
O(8)	2*i*	0.2808(3)	0.7281(3)	1.1773(2)	0.156(3)	0.129(2)	0.098(2)	0.086(2)	–0.041(2)	–0.016(2)
N(1)	2*i*	0.5284(1)	0.5718(1)	0.3068(1)	0.0392(9)	0.0384(9)	0.0349(9)	0.0181(8)	0.0093(7)	0.0025(7)
N(2)	2*i*	0.7141(2)	0.4214(2)	0.4181(1)	0.043(1)	0.045(1)	0.042(1)	0.0194(9)	0.0087(8)	0.0074(8)
N(3)	2*i*	0.7701(2)	0.5733(2)	0.3280(1)	0.040(1)	0.041(1)	0.049(1)	0.0147(9)	0.0133(8)	0.0123(9)
N(4)	2*i*	0.5590(2)	0.6459(2)	0.1014(1)	0.038(1)	0.045(1)	0.040(1)	0.0077(9)	0.0044(9)	0.0040(8)
N(5)	2*i*	0.3598(1)	0.5285(1)	0.0544(1)	0.041(1)	0.045(1)	0.0356(9)	0.0135(8)	0.0060(8)	–0.0006(8)
N(6)	2*i*	0.4522(2)	0.7410(1)	0.4850(1)	0.055(1)	0.043(1)	0.0385(9)	0.0278(9)	0.0127(8)	0.0069(8)
N(7)	2*i*	0.6038(2)	0.8102(2)	0.4010(1)	0.046(1)	0.041(1)	0.050(1)	0.0161(9)	0.0181(9)	0.0041(9)
N(8)	2*i*	0.2095(2)	0.2238(2)	0.3796(2)	0.054(1)	0.049(1)	0.089(2)	0.014(1)	–0.008(1)	0.009(1)
N(9)	2*i*	0.3282(3)	0.8035(3)	1.1201(2)	0.106(2)	0.132(3)	0.083(2)	0.081(2)	–0.019(2)	–0.044(2)
C(1)	2*i*	0.5761(2)	0.5212(2)	0.3923(2)	0.041(1)	0.040(1)	0.037(1)	0.017(1)	0.010(1)	0.007(1)
C(2)	2*i*	0.4389(2)	0.6094(2)	0.3351(2)	0.038(1)	0.042(1)	0.042(1)	0.016(1)	0.010(1)	0.005(1)
C(3)	2*i*	0.4710(2)	0.4878(2)	0.2129(2)	0.042(1)	0.038(1)	0.040(1)	0.014(1)	0.009(1)	0.001(1)
C(4)	2*i*	0.6854(2)	0.5047(2)	0.3779(1)	0.036(1)	0.034(1)	0.034(1)	0.0113(9)	0.0055(9)	0.0021(9)
C(5)	2*i*	0.8247(2)	0.4373(2)	0.3918(2)	0.044(1)	0.054(1)	0.045(1)	0.024(1)	0.005(1)	–0.002(1)
C(6)	2*i*	0.8950(3)	0.3740(3)	0.4110(2)	0.069(2)	0.077(2)	0.070(2)	0.047(2)	0.011(1)	0.009(2)
C(7)	2*i*	0.9988(3)	0.4122(3)	0.3709(2)	0.069(2)	0.109(3)	0.094(2)	0.062(2)	0.010(2)	–0.004(2)
C(8)	2*i*	1.0340(3)	0.5084(3)	0.3140(2)	0.054(2)	0.113(3)	0.085(2)	0.038(2)	0.022(2)	–0.004(2)
C(9)	2*i*	0.9657(2)	0.5707(3)	0.2946(2)	0.046(2)	0.080(2)	0.066(2)	0.023(2)	0.019(1)	0.007(2)
C(10)	2*i*	0.8601(2)	0.5330(2)	0.3348(2)	0.038(1)	0.052(1)	0.048(1)	0.018(1)	0.009(1)	0.001(1)
C(11)	2*i*	0.4615(2)	0.5532(2)	0.1221(1)	0.042(1)	0.037(1)	0.035(1)	0.014(1)	0.010(1)	–0.0020(9)
C(12)	2*i*	0.3945(2)	0.6110(2)	–0.0164(1)	0.047(1)	0.045(1)	0.033(1)	0.021(1)	0.009(1)	–0.0031(9)
C(13)	2*i*	0.3251(2)	0.6279(2)	–0.1039(2)	0.053(2)	0.064(2)	0.041(1)	0.029(1)	0.002(1)	–0.005(1)
C(14)	2*i*	0.3848(3)	0.7192(2)	–0.1580(2)	0.080(2)	0.071(2)	0.038(1)	0.046(2)	0.009(1)	0.008(1)
C(15)	2*i*	0.5091(3)	0.7928(2)	–0.1274(2)	0.084(2)	0.056(2)	0.049(2)	0.033(2)	0.022(1)	0.016(1)
C(16)	2*i*	0.5796(2)	0.7777(2)	–0.0414(2)	0.059(2)	0.053(2)	0.047(1)	0.015(1)	0.013(1)	0.010(1)
C(17)	2*i*	0.5195(2)	0.6851(2)	0.0131(1)	0.048(1)	0.043(1)	0.033(1)	0.018(1)	0.008(1)	0.0007(9)
C(18)	2*i*	0.4990(2)	0.7195(2)	0.4083(1)	0.043(1)	0.039(1)	0.039(1)	0.022(1)	0.0102(9)	0.0084(9)
C(19)	2*i*	0.6290(2)	0.8986(2)	0.4779(2)	0.053(1)	0.036(1)	0.051(1)	0.021(1)	0.007(1)	0.006(1)
C(20)	2*i*	0.7260(2)	1.0106(2)	0.5051(2)	0.065(2)	0.045(2)	0.074(2)	0.018(1)	0.007(2)	0.006(1)
C(21)	2*i*	0.7199(3)	1.0769(3)	0.5860(2)	0.098(2)	0.043(2)	0.078(2)	0.023(2)	–0.010(2)	–0.010(2)
C(22)	2*i*	0.6239(3)	1.0345(3)	0.6372(2)	0.120(3)	0.063(2)	0.052(2)	0.052(2)	0.003(2)	–0.007(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(23)	2*i*	0.5298(3)	0.9241(2)	0.6111(2)	0.090(2)	0.058(2)	0.045(1)	0.043(2)	0.017(1)	0.007(1)
C(24)	2*i*	0.5337(2)	0.8553(2)	0.5300(2)	0.062(1)	0.043(1)	0.038(1)	0.032(1)	0.008(1)	0.008(1)
C(25)	2*i*	−0.1584(2)	−0.1511(2)	0.2500(2)	0.042(1)	0.054(2)	0.061(2)	0.011(1)	0.015(1)	0.014(1)
C(26)	2*i*	−0.0323(2)	−0.0619(2)	0.2422(2)	0.039(1)	0.040(1)	0.057(1)	0.012(1)	0.014(1)	0.010(1)
C(27)	2*i*	0.0205(2)	−0.0745(2)	0.1624(2)	0.062(2)	0.048(2)	0.086(2)	0.011(1)	0.031(2)	−0.002(1)
C(28)	2*i*	0.1348(3)	0.0110(3)	0.1536(3)	0.079(2)	0.068(2)	0.118(3)	0.019(2)	0.064(2)	0.006(2)
C(29)	2*i*	0.1963(2)	0.1086(2)	0.2236(2)	0.047(2)	0.051(2)	0.122(3)	0.010(1)	0.037(2)	0.014(2)
C(30)	2*i*	0.1436(2)	0.1189(2)	0.3028(2)	0.040(1)	0.039(1)	0.076(2)	0.012(1)	0.004(1)	0.009(1)
C(31)	2*i*	0.0310(2)	0.0362(2)	0.3141(2)	0.043(1)	0.048(1)	0.056(1)	0.017(1)	0.012(1)	0.013(1)
C(32)	2*i*	−0.0853(3)	0.6613(2)	0.8961(2)	0.076(2)	0.070(2)	0.064(2)	0.033(2)	−0.002(2)	0.008(2)
C(33)	2*i*	0.0515(2)	0.7398(2)	0.9215(2)	0.044(1)	0.062(2)	0.081(2)	0.024(1)	0.008(1)	0.001(1)
C(34)	2*i*	0.1019(3)	0.8223(3)	0.8575(3)	0.062(2)	0.074(2)	0.106(3)	0.031(2)	0.009(2)	0.022(2)
C(35)	2*i*	0.2231(3)	0.9004(3)	0.8795(3)	0.071(2)	0.069(2)	0.118(3)	0.024(2)	0.023(2)	0.025(2)
C(36)	2*i*	0.2976(3)	0.8953(3)	0.9657(3)	0.048(2)	0.068(2)	0.108(3)	0.018(2)	0.019(2)	−0.013(2)
C(37)	2*i*	0.2483(2)	0.8106(2)	1.0299(2)	0.058(2)	0.074(2)	0.068(2)	0.041(2)	−0.001(1)	−0.018(2)
C(38)	2*i*	0.1245(2)	0.7331(2)	1.0096(2)	0.067(2)	0.053(2)	0.072(2)	0.026(2)	0.024(2)	0.001(1)

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References

1. Ji, B.-M.; Du, C.-X.; Zhu, Y.; Ding, K.-L.: Molecular assembly in an inclusion crystal of tris(2-benzimidazylmethyl)amine with 4-nitrobenzoic acid. J. Chem. Crystallogr. **30** (2000) 783-787.
2. Thompson, L. K.; Ramaswamy, B. S.; Seymour, E. A.: Cobalt(II) and Zinc(II) Complexes of Tripod Ligand Tris(2-benzimidazylmethyl)amine - Some 5-Coordinate Derivatives and Some with Mixed Stereochemistries. Can. J. Chem. **55** (1977) 878-888.
3. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXTL. Structure Determination Software Programs. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1990.
6. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. J. Appl. Crystallogr. **32** (1999) 837-838.