Crystal structure of benzylammonium 2, 3, 4, 5-tetrabromo-6-(methoxycarbonyl)benzoate, $(C_7H_{10}N)^+(C_9H_3Br_4O_4)^-$, $C_{16}H_{13}Br_4NO_4$

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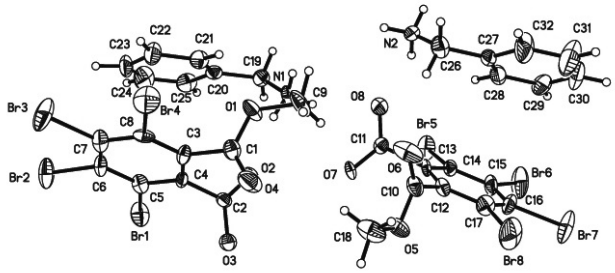

Abstract

$C_{16}H_{13}Br_4No_4$, monoclinic, $P2_1/c$ (no. 14), a = 18.883(2) Å, b = 16.095(2) Å, c = 14.023(1) Å, β = 109.785(1)°, V = 4010.5 Å^3, Z = 8, $R_{gt}(F)$ = 0.0533, $wR_{ref}(F^2)$ = 0.1064, T = 298 K.

Source of material

All the reagents and solvents from commercial sources were used without further purification. A mixture of 4,5,6,7-tetrabromo-isobenzofuran-1,3-dione (4.64 g, 0.01 mol) and methanol (15 ml) was refluxed for 0.5 h. Then benzylamine (1.07 g, 0.01 mol) was added to the above solution and mixed for 0.5 h at room temperature. After filtration and drying, the title compound was obtained. 20 mg of that was dissolved in 20 ml methanol, and the solution was kept at room temperature for 6 d. Isothermal evaporation at RT gave colourless single crystals of the title compound, suitable for *X*-ray analysis.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.13×0.30×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	80.47 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19693, 7072
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2503
$N(param)_{refined}$:	455
Programs:	SHELXS-97 [4]

Discussion

Tetrabromphthalimide and its derivatives have been found to be useful flame retardants in polyesters, e.g. polybutylene terephthalate, and other resin formulations [1]. In the present work, the reaction of tetrabromophthalic anhydride and benzylamine in methanol is expected to form 2-benzyl-4,5,6,7-tetrabromo-isoindoline-1,3-dione, but instead the title compound formed, and this may have occured because of the reduced time and temperature of the reaction. In this paper, the crystal structure of the title compound is reported.

The asymmetric unit of the title compound contains two benzylammonium cations and two 2,3,4,5-tetrabromo-6-(methoxycarbonyl)benzoate anions. In one anion, the dihedral angles formed by the benzene ring and the mean planes of the carboxylate and methoxycarbonyl groups are 77.3(2) and 81.1(2)°, respectively, while the dihedral angles formed by the benzene ring and the mean planes of the carboxylate and methoxycarbonyl groups are 64.9(2) and 72.3(2)°, respectively in the other one. In one cation, atom N1 is displaced by 0.840(2) Å from the benzene ring, while atom N2 is displaced by -0.680 (2) Å from the benzene ring in the other one. The bond lengths and angles are in agreement with those of the ethyl-ammonium 2-(methoxycarbonyl)-3,4,5,6-tetrabromobenzoate methanol solvate [2] and of the 2-methylanilinium 3,4,5,6-tetra-bromo-2-(methoxycarbonyl)benzoate methanol monosolvate [3]. The crystal structure is stabilized by N–H···O hydrogen bonds.

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.5415	0.7194	0.3853	0.081
H(1B)	4*e*	0.6008	0.6650	0.4467	0.081
H(1C)	4*e*	0.5409	0.6909	0.4834	0.081
H(2A)	4*e*	0.7032	0.8007	0.2374	0.082
H(2B)	4*e*	0.6481	0.8124	0.2877	0.082
H(2C)	4*e*	0.7175	0.7675	0.3386	0.082
H(9A)	4*e*	0.5483	0.9511	0.5061	0.125
H(9B)	4*e*	0.5416	0.8981	0.4096	0.125
H(9C)	4*e*	0.5933	0.8678	0.5168	0.125
H(18A)	4*e*	0.7366	0.9686	0.7328	0.120
H(18B)	4*e*	0.7253	0.9156	0.8203	0.120
H(18C)	4*e*	0.6739	0.9002	0.7078	0.120
H(19A)	4*e*	0.5291	0.5540	0.4177	0.061
H(19B)	4*e*	0.5093	0.5973	0.3118	0.061
H(21)	4*e*	0.4113	0.7316	0.3514	0.063
H(22)	4*e*	0.2813	0.7332	0.3302	0.081
H(23)	4*e*	0.2287	0.6128	0.3696	0.083
H(24)	4*e*	0.2925	0.4894	0.3865	0.096
H(25)	4*e*	0.4178	0.4885	0.4032	0.075
H(26A)	4*e*	0.7254	0.8975	0.4043	0.074
H(26B)	4*e*	0.7108	0.9330	0.2953	0.074
H(28)	4*e*	0.8390	0.7677	0.3894	0.069
H(29)	4*e*	0.9702	0.7744	0.4219	0.086
H(30)	4*e*	1.0205	0.9049	0.4058	0.153
H(31)	4*e*	0.9480	1.0191	0.3620	0.171
H(32)	4*e*	0.8200	1.0075	0.3278	0.120

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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}
Br(1)	4*e*	0.39540(6)	0.57220(6)	0.71014(9)	0.0679(7)	0.0408(6)	0.102(1)	0.0011(6)	0.0414(8)	0.0187(7)
Br(2)	4*e*	0.21888(6)	0.63783(7)	0.6246(1)	0.0499(7)	0.0751(8)	0.145(1)	–0.0236(7)	0.0493(8)	–0.0126(9)
Br(3)	4*e*	0.18010(6)	0.81999(8)	0.5147(1)	0.0383(7)	0.109(1)	0.155(1)	0.0253(8)	0.0125(8)	0.019(1)
Br(4)	4*e*	0.31705(6)	0.93616(7)	0.49151(9)	0.0878(9)	0.0514(7)	0.104(1)	0.0206(7)	0.0279(8)	0.0279(8)
Br(5)	4*e*	0.84802(6)	0.55170(6)	0.52886(9)	0.0627(7)	0.0494(7)	0.112(1)	0.0003(6)	0.0409(8)	–0.0162(7)
Br(6)	4*e*	1.02581(6)	0.60446(7)	0.6137(1)	0.0455(7)	0.0878(9)	0.192(2)	0.0214(7)	0.0519(9)	0.020(1)
Br(7)	4*e*	1.07577(6)	0.78396(9)	0.7289(1)	0.0403(7)	0.140(1)	0.176(2)	–0.0345(9)	0.0121(9)	–0.011(1)
Br(8)	4*e*	0.94456(7)	0.91166(8)	0.7508(1)	0.111(1)	0.087(1)	0.150(2)	–0.0559(9)	0.053(1)	–0.053(1)
N(1)	4*e*	0.5521(4)	0.6770(4)	0.4286(5)	0.034(5)	0.082(6)	0.056(6)	0.005(5)	0.027(5)	0.012(5)
N(2)	4*e*	0.6970(3)	0.8093(5)	0.2968(5)	0.034(5)	0.092(7)	0.036(6)	–0.003(5)	0.008(5)	0.007(5)
O(1)	4*e*	0.4844(3)	0.8508(4)	0.4924(5)	0.077(5)	0.067(5)	0.057(5)	–0.019(4)	0.048(5)	–0.015(4)
O(2)	4*e*	0.5155(4)	0.8967(5)	0.6511(6)	0.110(7)	0.106(7)	0.058(6)	–0.060(6)	0.043(6)	–0.022(5)
O(3)	4*e*	0.5415(3)	0.7057(4)	0.7755(5)	0.042(4)	0.071(5)	0.045(5)	0.015(4)	0.017(4)	–0.003(4)
O(4)	4*e*	0.5410(3)	0.6723(5)	0.6208(5)	0.046(4)	0.152(7)	0.047(5)	0.023(5)	0.029(4)	–0.001(5)
O(5)	4*e*	0.7772(3)	0.8534(4)	0.7400(5)	0.084(5)	0.049(4)	0.056(5)	0.018(4)	0.044(5)	0.008(4)
O(6)	4*e*	0.7432(4)	0.8848(4)	0.5762(6)	0.123(7)	0.069(5)	0.069(7)	0.054(5)	0.056(6)	0.027(5)
O(7)	4*e*	0.7013(3)	0.6872(4)	0.6028(5)	0.033(4)	0.167(8)	0.054(5)	–0.014(4)	0.030(4)	0.008(5)
O(8)	4*e*	0.7106(3)	0.6893(4)	0.4495(6)	0.051(5)	0.069(5)	0.050(5)	–0.005(4)	0.021(5)	–0.004(5)
C(1)	4*e*	0.4756(5)	0.8559(6)	0.5804(9)	0.048(7)	0.037(6)	0.06(1)	–0.006(6)	0.024(8)	–0.001(6)
C(2)	4*e*	0.5107(5)	0.6985(6)	0.6795(8)	0.043(7)	0.045(6)	0.031(8)	–0.013(5)	0.016(7)	–0.004(6)
C(3)	4*e*	0.4111(5)	0.8029(5)	0.5892(7)	0.027(6)	0.028(6)	0.055(8)	–0.002(5)	0.012(6)	–0.006(6)
C(4)	4*e*	0.4291(5)	0.7263(5)	0.6378(6)	0.021(5)	0.037(6)	0.037(7)	0.001(5)	0.010(5)	–0.002(5)
C(5)	4*e*	0.3702(5)	0.6774(5)	0.6462(7)	0.049(6)	0.029(5)	0.056(8)	0.003(5)	0.026(6)	–0.004(5)
C(6)	4*e*	0.2965(5)	0.7048(6)	0.6098(8)	0.032(6)	0.049(7)	0.070(9)	–0.010(6)	0.025(6)	–0.005(7)
C(7)	4*e*	0.2789(5)	0.7819(6)	0.5627(8)	0.044(7)	0.059(7)	0.072(9)	–0.007(6)	0.028(7)	–0.005(7)
C(8)	4*e*	0.3386(6)	0.8309(5)	0.5543(6)	0.065(7)	0.028(5)	0.026(7)	0.013(6)	0.014(6)	0.013(5)
C(9)	4*e*	0.5472(5)	0.8958(5)	0.4802(7)	0.105(9)	0.079(8)	0.10(1)	–0.039(7)	0.072(8)	0.004(7)
C(10)	4*e*	0.7822(6)	0.8478(6)	0.648(1)	0.052(8)	0.042(7)	0.07(1)	0.000(6)	0.029(8)	0.014(7)
C(11)	4*e*	0.7364(5)	0.6937(5)	0.5428(9)	0.033(7)	0.041(6)	0.044(8)	0.007(5)	0.014(7)	–0.004(6)
C(12)	4*e*	0.8428(5)	0.7877(6)	0.6438(7)	0.040(7)	0.035(6)	0.054(8)	0.004(6)	0.025(6)	0.009(6)
C(13)	4*e*	0.8218(4)	0.7140(5)	0.5938(7)	0.018(5)	0.031(6)	0.051(7)	0.004(5)	0.018(5)	0.014(5)
C(14)	4*e*	0.8771(5)	0.6579(5)	0.5874(7)	0.036(6)	0.040(6)	0.047(7)	–0.008(5)	0.014(6)	0.007(6)
C(15)	4*e*	0.9530(5)	0.6796(6)	0.6278(8)	0.028(6)	0.068(8)	0.075(9)	0.006(6)	0.023(7)	0.018(7)
C(16)	4*e*	0.9742(5)	0.7553(6)	0.6775(8)	0.036(7)	0.053(7)	0.066(9)	–0.017(6)	0.004(6)	0.000(7)
C(17)	4*e*	0.9188(6)	0.8077(6)	0.6842(8)	0.064(8)	0.037(6)	0.065(9)	–0.008(6)	0.025(7)	–0.006(6)
C(18)	4*e*	0.7237(5)	0.9147(5)	0.7512(7)	0.110(9)	0.076(8)	0.072(9)	0.047(8)	0.053(8)	0.011(7)
C(19)	4*e*	0.5069(5)	0.6033(5)	0.3794(7)	0.045(6)	0.055(7)	0.050(8)	0.004(6)	0.015(6)	0.006(6)
C(20)	4*e*	0.4242(5)	0.6087(6)	0.3720(7)	0.047(7)	0.043(6)	0.029(7)	–0.006(6)	0.010(6)	–0.008(6)
C(21)	4*e*	0.3865(5)	0.6828(6)	0.3564(7)	0.060(8)	0.044(7)	0.053(8)	–0.012(6)	0.017(7)	–0.001(6)
C(22)	4*e*	0.3093(6)	0.6846(7)	0.3479(7)	0.045(7)	0.074(8)	0.08(1)	–0.004(7)	0.021(7)	0.006(7)
C(23)	4*e*	0.2772(6)	0.6119(8)	0.3667(8)	0.039(7)	0.10(1)	0.075(9)	–0.024(8)	0.029(7)	–0.013(9)
C(24)	4*e*	0.3164(7)	0.5389(7)	0.3811(9)	0.08(1)	0.058(8)	0.10(1)	–0.031(8)	0.031(9)	0.001(8)
C(25)	4*e*	0.3905(6)	0.5378(6)	0.3878(7)	0.072(9)	0.044(7)	0.063(8)	–0.016(7)	0.013(8)	0.003(6)
C(26)	4*e*	0.7339(5)	0.8877(6)	0.3408(8)	0.057(7)	0.063(8)	0.072(9)	–0.004(6)	0.033(7)	–0.006(7)
C(27)	4*e*	0.8176(5)	0.8881(7)	0.3599(7)	0.036(7)	0.062(7)	0.046(8)	0.000(7)	0.012(6)	0.019(7)
C(28)	4*e*	0.8613(5)	0.8183(6)	0.3848(7)	0.045(8)	0.066(8)	0.065(8)	–0.002(6)	0.022(7)	0.014(7)
C(29)	4*e*	0.9399(6)	0.8213(7)	0.4038(8)	0.037(7)	0.097(9)	0.072(9)	0.018(7)	0.005(7)	0.013(8)
C(30)	4*e*	0.9691(7)	0.900(1)	0.394(1)	0.046(9)	0.19(2)	0.13(1)	–0.05(1)	0.01(1)	0.02(1)
C(31)	4*e*	0.9267(8)	0.9680(9)	0.368(1)	0.07(1)	0.12(1)	0.21(2)	–0.03(1)	–0.00(1)	0.04(1)
C(32)	4*e*	0.8502(7)	0.9607(7)	0.3488(9)	0.067(9)	0.069(8)	0.15(1)	–0.019(8)	0.023(9)	0.042(9)

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