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Diisopropylammonium methanesulfonate

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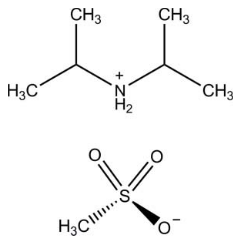
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.027; wR factor = 0.060; data-to-parameter ratio = 21.6.

The title molecular salt, $C_6H_{16}N^+\cdot CH_3SO_3^-$, has been determined at 150 K. Two diisopropylammonium cations (dipH) and two anions form N—H⋯O hydrogen-bonded cyclic dimers lying around centers of symmetry. Only two of the three O atoms of the methanesulfonate anion are involved in hydrogen bonding, resulting in slightly longer S—O bond lengths. The title structure represents an example of a sulfonate anion that is part of a hydrogen-bonding $R_4^4(12)$ graph-set motif, which is well known for related dipH acetates. Additionally, the Raman and the IR spectroscopic data for the title compound are presented.

Related literature

For simple dipH salts, see: Bajorat & Reiss (2007); Reiss (1998, 2002); Reiss (2010*a*,*b*); Reiss & Engel (2004); Reiss & Meyer (2010); Sada *et al.* (2004), Summers *et al.* (1998). For spectroscopic data for sulfonate salts, see: Thomson (1972); Genceli Guner *et al.* (2010). For graph-set analysis, see: Etter *et al.* (1990).



Experimental

Crystal data

$C_6H_{16}N^+\cdot CH_3SO_3^-$
M_r = 197.29
Monoclinic, $P2_1/n$
a = 8.88154 (13) Å
b = 8.53537 (13) Å
c = 14.5784 (2) Å
β = 101.8161 (15)°
V = 1081.73 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 150 K
0.65 × 0.25 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.951, T_{max} = 1.000
25064 measured reflections
3149 independent reflections
2782 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.060
S = 1.03
3149 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4433 (9)	S1—O3	1.4600 (8)
S1—O1	1.4596 (8)	S1—C1	1.7560 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H11⋯O1	0.885 (13)	1.944 (13)	2.8168 (11)	168.5 (12)
N1—H12⋯O3^i	0.891 (13)	1.919 (13)	2.7944 (11)	166.9 (12)

Symmetry code: (i) $-x+1, -y, -z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2018).

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supplementary materials

Acta Cryst. (2011). E**67**, o2169   [**doi:10.1107/S1600536811029382**]

Diisopropylammonium methanesulfonate

G. J. Reiss and **M. K. Meyer**

Comment

More than one hundred structures are listed to date in the Cambridge Crystallographic Database, which include a diisopropylammonium cation (dipH). In most cases the dipH cation is the counter cation of bigger anionic species *e.g.* anionic complexes and clusters. A limited number of structures are reported that are solely constructed by small classical anions and the dipH cation. In these cases the structure type is strongly dependent on the geometry and the ability of these anions to form hydrogen bonds. The structures reported so far range from a quasi-molecular $(dipH)_2[SiF_6]$ (Reiss, 1998), over cyclic dimers for some acetates (*e.g.*: Sada *et al.*, 2004) and *e.g.* a substituted phosphate (Summers *et al.*, 1998), to one-dimensional polymers for the halogenides and some pseudo-halogenides (literature cited in Reiss & Meyer, 2010). Even a two-dimensional hydrogen bonded network for the $(dipH)_2SO_4$ (Reiss & Engel, 2004) and three-dimensional networks for $dipH[IrCl_6]$ (Reiss, 2002) and $(dipH)_2[CdCl_4]$ (Reiss, 2010*a*) have been reported. The asymmetric unit of the title compound, which crystallizes in the centrosymmetric space group $P2_1/n$, consists of one formular unit. The structure is composed of centrosymmetric, hydrogen bonded, cyclic dimers which are composed of two dipH cations and two methanesulfonate anions arranged as rings (Fig. 1). The graph set (Etter *et al.*, 1990) for these hydrogen bonded dimers is $R_4^4(12)$. All N–C, C–C, S–O, and S–C bond lengths are generally within the expected range. The two S–O bond lengths of the oxygen atoms involved in hydrogen bonding (O1 and O3) are longer than the third one which is in accord to our anticipation (Table 1). The N–H···O hydrogen bonds with donor-acceptor distances close to 2.79–2.82 Å (Table 2) are in the range of medium strong hydrogen bonds. The $R_4^4(12)$ hydrogen bonding motif is well known for dipH acetates (Reiss & Meyer, 2010, Sada *et al.* 2004). Combinations of the dipH cation with structurally similar anions like $[NO_3]^-$ (Reiss, 2010*b*), $[ClO_4]^-$ (Bajorat & Reiss, 2007) and various substituted carboxylate anions can be described as the generalized synthon: $\{dipH\}^+\{O_2XR_y\}^-$ (X = C, Cl, N; y = 1,2, R = O, C). The title structure is a further example with this supramolecular synthon and the typical cyclic dimer.

Experimental

Diisopropylammonium methanesulfonate, $((CH_3)_2CH)_2NH_2[CH_3SO_3]$ was prepared by the reaction of 0.72 g (7.12 mmol) diisopropylamine and 1.48 g (15.40 mmol) methanesulfonic acid at room temperature. From colourless solution small block-shaped crystals were obtained within a few days. A Raman spectrum was measured using a Bruker MULTIRAM spectrometer; Nd:YAG-Laser at 1064 nm; RT-InGaAS-detector; 4000–70 cm^{-1}: 3022(sh), 2986(ν(C–H), s), 2944(ν(C–H), *vs*), 2784(ν(N–H), w), 1462 (δ(C–H, m), 1429(δ(C–H, m), 1350(w), 1315(w), 1227(w), 1183(w), 1158(w), 1099 (w), 1044 (ν(S–O),*vs*), 958 (w), 914(w), 808(*s*), 778(ν(C–S), s), 558(δ(S–O), s), 528(*m*), 470(*m*), 392(w), 348(ρ(S–O), br), 83(*m*). IR data collected on a Digilab FT3400 spectrometer using a MIRacle ATR unit (Pike Technologies); 4000–560 cm^{-1}: 3019(ν(C–H), s), 2988 (sh), 2941(*m*), 2870(ν(C–H), s), 2781(ν(N–H), m), 2514(*m*), 1625(w), 1601(w), 1483(δ(C–H, m), 1416(w), 1397(*m*), 1331(w), 1314(w), 1206(*vs*), 1177(sh), 1153(ν_s(S–O), *vs*), 1100(*m*), 1040(ν_a(S–O), *vs*), 977(w), 954(w), 837(w), 805(w), 776(ν(C–S), s), 551(δ(S–O)s). Band assignments for Raman and IR spectroscopic data were made by comparing results of earlier work done on sodium- and caesium methanesulfonate (Thomson, 1972), magnesium sulfonate (Genceli Guner *et al.*, 2010) and dipHCl (Reiss & Meyer 2010).

Refinement

A single-crystal suitable for structure determination was harvested from the mother liquor and directly transferred into the cooling stream of an Oxford-Xcalibur diffractometer equipped with an EOS-CCD detector. Data collection was performed at 150 K. All hydrogen atoms were located *via* difference Fourier synthesis. Positional parameters of hydrogen atoms of the NH_2 and the CH group were refined freely. All hydrogen atoms belonging to methyl groups were refined using a riding model with restrained angles and C–H distances but allowed to rotate about the C–C bond. Anisotrope displacement parameters of all non hydrogen atoms and individual isotropic displacement parameters for all hydrogen atoms were refined freely.

Figures

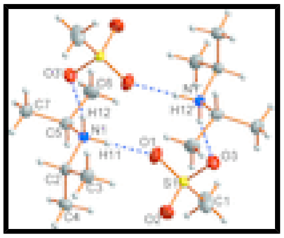

Fig. 1. Hydrogen atoms are drawn with an arbitrary radius and the displacement ellipsoids are shown at the 50% probability level; ' = 1 - *x*,-*y*,-*z*.

Diisopropylammonium methanesulfonate

Crystal data

$C_6H_{16}N^+\cdot CH_3SO_3^-$

M_r = 197.29

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

a = 8.88154 (13) Å

b = 8.53537 (13) Å

c = 14.5784 (2) Å

β = 101.8161 (15)°

V = 1081.73 (3) Å^3

Z = 4

$F(000)$ = 432

D_x = 1.211 Mg m^{-3}

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 18202 reflections

θ = 3.4–32.0°

μ = 0.27 mm^{-1}

T = 150 K

Needle, colourless

0.65 × 0.25 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 16.27 pixels mm^{-1}

ω scans

Absorption correction: multi-scan

3149 independent reflections

2782 reflections with $I > 2\sigma(I)$

R_{int} = 0.024

$\theta_{\text{max}} = 30.0°$, $\theta_{\text{min}} = 4.1°$

$h = -12 \rightarrow 12$

$k = -12 \rightarrow 12$

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.951$, $T_{\max} = 1.000$

25064 measured reflections

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.060$

$S = 1.03$

3149 reflections

146 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.55P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.34$ e Å^{-3}

$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0276 (9)

Special details

Experimental. CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.52, Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.38147 (3)	0.02594 (3)	0.180331 (16)	0.01976 (7)
O1	0.47025 (9)	0.13813 (10)	0.13749 (6)	0.0355 (2)
O2	0.47472 (10)	−0.09928 (12)	0.22849 (6)	0.0408 (2)
O3	0.24712 (9)	−0.03058 (10)	0.11340 (5)	0.02989 (17)
C1	0.30699 (15)	0.12931 (19)	0.26524 (9)	0.0442 (3)
H1A	0.2477	0.0595	0.2955	0.065 (5)*
H1B	0.2424	0.2128	0.2357	0.062 (5)*
H1C	0.3901	0.1721	0.3109	0.066 (5)*
N1	0.74609 (9)	0.09843 (10)	0.07323 (6)	0.01840 (16)
H11	0.6562 (15)	0.0976 (15)	0.0906 (9)	0.028 (3)*
H12	0.7329 (14)	0.0729 (15)	0.0128 (9)	0.028 (3)*

C2	0.84677 (11)	−0.02552 (12)	0.12848 (7)	0.02104 (18)
H2	0.9413 (14)	−0.0236 (14)	0.1056 (8)	0.022 (3)*
C3	0.76690 (13)	−0.18212 (12)	0.10422 (8)	0.0283 (2)
H3A	0.6709	−0.1827	0.1248	0.036 (4)*
H3B	0.8313	−0.2649	0.1349	0.039 (4)*
H3C	0.7480	−0.1977	0.0376	0.037 (4)*
C4	0.87442 (13)	0.00990 (14)	0.23269 (7)	0.0286 (2)
H4A	0.9296	0.1069	0.2452	0.036 (4)*
H4B	0.9337	−0.0731	0.2670	0.037 (4)*
H4C	0.7775	0.0183	0.2517	0.037 (4)*
C5	0.80229 (12)	0.26542 (12)	0.08130 (7)	0.02175 (19)
H5	0.8146 (13)	0.2921 (14)	0.1445 (8)	0.022 (3)*
C6	0.67707 (14)	0.36632 (13)	0.02325 (8)	0.0322 (2)
H6A	0.6606	0.3347	−0.0412	0.041 (4)*
H6B	0.7081	0.4742	0.0286	0.049 (4)*
H6C	0.5834	0.3538	0.0457	0.041 (4)*
C7	0.95364 (13)	0.27936 (14)	0.04905 (8)	0.0296 (2)
H7A	1.0290	0.2129	0.0868	0.041 (4)*
H7B	0.9884	0.3861	0.0553	0.042 (4)*
H7C	0.9393	0.2479	−0.0154	0.036 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01698 (10)	0.02503 (12)	0.01773 (10)	0.00188 (9)	0.00463 (8)	−0.00071 (9)
O1	0.0289 (4)	0.0331 (4)	0.0485 (5)	−0.0013 (3)	0.0171 (4)	0.0074 (4)
O2	0.0310 (4)	0.0471 (5)	0.0445 (5)	0.0131 (4)	0.0083 (4)	0.0205 (4)
O3	0.0267 (4)	0.0403 (4)	0.0216 (3)	−0.0034 (3)	0.0022 (3)	−0.0084 (3)
C1	0.0305 (6)	0.0663 (9)	0.0370 (6)	−0.0021 (6)	0.0101 (5)	−0.0286 (7)
N1	0.0188 (4)	0.0194 (4)	0.0171 (4)	−0.0008 (3)	0.0040 (3)	−0.0005 (3)
C2	0.0193 (4)	0.0209 (4)	0.0238 (4)	0.0026 (4)	0.0064 (3)	0.0024 (4)
C3	0.0306 (5)	0.0205 (5)	0.0350 (6)	−0.0003 (4)	0.0096 (4)	0.0007 (4)
C4	0.0295 (5)	0.0322 (6)	0.0223 (5)	0.0020 (4)	0.0009 (4)	0.0043 (4)
C5	0.0269 (5)	0.0187 (4)	0.0196 (4)	−0.0025 (4)	0.0045 (4)	−0.0015 (3)
C6	0.0368 (6)	0.0235 (5)	0.0360 (6)	0.0049 (4)	0.0067 (5)	0.0058 (4)
C7	0.0278 (5)	0.0295 (6)	0.0317 (5)	−0.0080 (4)	0.0066 (4)	0.0030 (4)

Geometric parameters (Å, °)

S1—O2	1.4433 (9)	C3—H3B	0.9600
S1—O1	1.4596 (8)	C3—H3C	0.9600
S1—O3	1.4600 (8)	C4—H4A	0.9600
S1—C1	1.7560 (12)	C4—H4B	0.9600
C1—H1A	0.9600	C4—H4C	0.9600
C1—H1B	0.9600	C5—C6	1.5196 (15)
C1—H1C	0.9600	C5—C7	1.5169 (14)
N1—C5	1.5068 (13)	C5—H5	0.934 (12)
N1—C2	1.5076 (12)	C6—H6A	0.9600
N1—H11	0.885 (13)	C6—H6B	0.9600

N1—H12	0.891 (13)	C6—H6C	0.9600
C2—C4	1.5189 (14)	C7—H7A	0.9600
C2—C3	1.5206 (14)	C7—H7B	0.9600
C2—H2	0.964 (12)	C7—H7C	0.9600
C3—H3A	0.9600		
O2—S1—O1	112.80 (5)	N1—C2—C4	110.58 (8)
O2—S1—O3	112.92 (6)	N1—C2—C3	107.17 (8)
O1—S1—O3	111.71 (5)	C4—C2—C3	112.32 (9)
O2—S1—C1	106.90 (7)	N1—C2—H2	105.4 (7)
O1—S1—C1	106.65 (7)	C4—C2—H2	111.6 (7)
O3—S1—C1	105.24 (5)	C3—C2—H2	109.4 (7)
C5—N1—C2	118.12 (8)	N1—C5—C6	107.44 (8)
C5—N1—H11	106.8 (9)	N1—C5—C7	110.51 (8)
C2—N1—H11	108.2 (8)	C6—C5—C7	112.14 (9)
C5—N1—H12	106.4 (8)	N1—C5—H5	106.1 (8)
C2—N1—H12	107.5 (8)	C6—C5—H5	109.6 (7)
H11—N1—H12	109.6 (11)	C7—C5—H5	110.8 (7)
C5—N1—C2—C4	59.81 (11)	C2—N1—C5—C6	−177.19 (8)
C5—N1—C2—C3	−177.47 (8)	C2—N1—C5—C7	60.18 (11)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O1	0.885 (13)	1.944 (13)	2.8168 (11)	168.5 (12)
N1—H12···O3^{i}	0.891 (13)	1.919 (13)	2.7944 (11)	166.9 (12)

Symmetry codes: (i) $-x+1, -y, -z$.

Fig. 1