Acta Cryst. (1983). C**39**, 1236–1237

Structure of *N*-Methylsulphamic Acid, CH_5NO_3S

BY ALAN J. MORRIS, COLIN H. L. KENNARD* AND JOHN R. HALL
Department of Chemistry, University of Queensland, Brisbane 4067, *Australia*

GRAHAM SMITH
Department of Chemistry, Queensland Institute of Technology, Brisbane 4000, *Australia*

AND ALLAN H. WHITE
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, *Australia*

(*Received* 3 *November* 1982; *accepted* 13 *April* 1983)

Abstract. $M_r = 111{\cdot}1$, rhombohedral, $R3c$, $a = 9{\cdot}38\,(1)$ Å, $\alpha = 108{\cdot}7\,(1)°$, $V = 652{\cdot}8$ Å^3, $Z = 6$, $D_m = 1{\cdot}65$, $D_x = 1{\cdot}70$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·54 mm^{-1}, $T = 293$ K, $F(000) = 348$; $R = 0{\cdot}035$ for 454 observed reflections. The compound was prepared from $K(CH_3)NH(SO_3)$ by ion exchange. The molecule has a central N tetrahedrally bonded to two H atoms, CH_3, and an SO_3 group. The N—S—O angle is smaller [102·4 (7)°] than that found for the comparative potassium salt [106·2 (2)°]. The N—S distance, 1·779 (8) Å, is intermediate between the distance found for $H_3N(SO_3)$ [1·76 (2) Å] and $H(CH_3)_2N(SO_3)$ [1·790 (6) Å] and much longer than in the potassium salt [1·637 (4) Å].

Introduction. The title compound, $H_2(CH_3)NSO_3$, is the last member of a series of sulphamic acids, with general formula $H_x(CH_3)_{3-x}N(SO_3)$, to be determined (Morris, Kennard, Hall & Smith, 1982).

Experimental. Prepared from $K(CH_3)NH(SO_3)$ by cation exchange on a column packed with Amberlite IR120(H) in the acid form; composition: found: C 11·0, H 4·6, N 12·7%; calculated for CH_5NO_3S: C 10·8, H 4·5, N 12·6%; D_m (flotation method); prismatic crystal (0·2 × 0·2 × 0·15 mm) enclosed in a Lindemann capillary, data collected on a Syntex $P2_1$ four-circle diffractometer; 13 high-angle reflections used to measure lattice parameters; systematic absences *hhl*, $l = 2n + 1$; analysis of equivalent reflections confirmed the Laue group and selected space group; no absorption corrections applied; $2\theta_{\max} = 50°$; hemisphere of reciprocal lattice collected; three standards used [200, I 708 900, $\sigma(I)$ 4700; 020, I 729 700, $\sigma(I)$ 4800; 002, I 721 700, $\sigma(I)$ 4700]; 649 reflections measured, 490 unique reflections; $R_{\rm int} = 0{\cdot}155$; 36 unobserved reflections [$I < 2\sigma(I)$]. Sharpened Patterson synthesis located S; F used in least squares; H atoms located in a difference Fourier map and refined isotropically; all other atomic and anisotropic thermal parameters refined; final R 0·035, R_w 0·043; least squares determined $w = 1/[\sigma^2(F_o) + 0{\cdot}004(F_o)^2]$; maximum least-squares shift-to-error ratio in final cycle 1·070; average shift-to-error ratio 0·2; maximum height in final difference Fourier map 0·18 e Å^{-3}; no corrections for secondary extinction; atomic scattering factors, non-hydrogen (Cromer & Mann, 1968), H (Stewart, Davidson & Simpson, 1965); computer program *SHELX* (Sheldrick, 1976).

Discussion. Final atomic parameters are given in Table 1.†

N-Methylsulphamic acid $[H_2(CH_3)N]^+(SO_3)^-$ (Fig. 1) is analogous to *N*,*N*-dimethylsulphamic acid $[H(CH_3)_2N]^+(SO_3)^-$ (Morris, Kennard, Hall & Smith, 1982) and sulphamic acid $[H_3N^+(SO_3)^-]$ (Sass, 1960).

Table 1. *Positional parameters* (×10^4, *for* H ×10^3) *and isotropic thermal parameters* (×10^4, *for* H ×10^2) *with e.s.d.'s in parentheses*

For non-H atoms $U_{\rm eq} = (U_{11}\,U_{22}\,U_{33})^{1/3}$.

	x	y	z	$U_{\rm eq}$ or $U_{\rm iso}$(Å^2)
S	1581	6397	2050	27 (1)
O(1)	2749 (7)	5752 (7)	2495 (8)	61 (4)
O(2)	1274 (6)	7237 (7)	3409 (6)	44 (3)
O(3)	131 (7)	5340 (7)	424 (7)	39 (3)
N	2751 (8)	8110 (8)	1777 (8)	26 (3)
C	1955 (13)	9241 (13)	1651 (14)	49 (5)
HN(1)	369 (11)	862 (11)	253 (11)	4 (2)
HN(2)	279 (12)	759 (12)	82 (14)	5 (3)
HC(1)	246 (11)	988 (13)	126 (13)	8 (3)
HC(2)	226 (15)	981 (16)	272 (17)	8 (5)
HC(3)	82 (16)	852 (16)	64 (16)	10 (3)

---

* To whom correspondence should be addressed.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38527 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/091236-02$01.50

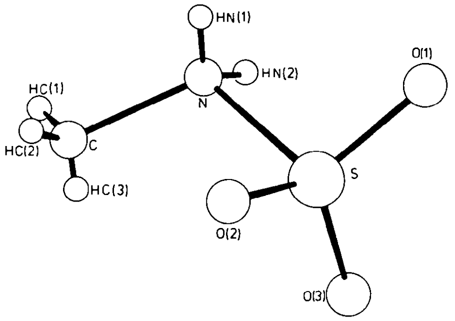

Fig. 1. The molecular stereochemistry and atom numbering.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for the system* $H_x(CH_3)_{3-x}N(SO_3)$ *with estimated standard deviations in parentheses*

	$(CH_3)_3N(SO_3)^a$	$H(CH_3)_2N(SO_3)^b$ (mean results)	$H_2(CH_3)N(SO_3)^c$ (mean results)	$H_3N(SO_3)^d$ (mean results)
N–S	1·844 (2)	1·790 (6)	1·779 (8)	1·76 (2)
N–C	1·496 (2)	1·504 (10)	1·493 (12)	—
S–O	1·405 (2)	1·430 (5)	1·425 (8)	1·44 (2)
C–N–C	109·1 (1)	111·5 (7)	—	—
S–N–C	109·8 (1)	112·3 (5)	113·4 (9)	—
H–N–S	—	96 (4)	106 (2)	111·3
H–N–C	—	112 (3)	112 (2)	—
N–S–O	101·8 (1)	102·1 (3)	102·4 (7)	103·2 (2)
O–S–O	115·9 (1)	115·8 (4)	115·4 (6)	115·1 (2)

Notes: (*a*) Morris, Kennard, Hall, Smith & White (1983); (*b*) Morris, Kennard, Hall & Smith (1982); (*c*) this work; (*d*) Sass (1960).

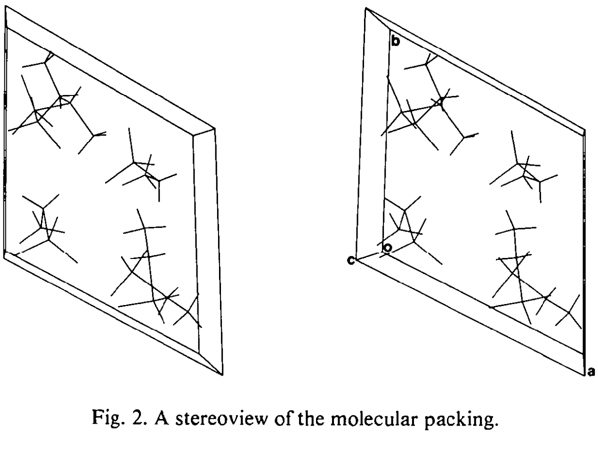

Fig. 2. A stereoview of the molecular packing.

All three compounds exist as zwitterions with tetrahedral configuration about the N atom and comparable bond distances and angles. A comparison of mean interatomic distances for the nitrogen sulphonate series is found in Table 2. The N—S distance [1·779 (8) Å] is intermediate between that for $H_3N(SO_3)$ [1·76 (2) Å (Sass, 1960)] and $H(CH_3)_2N(SO_3)$ [1·790 (6) Å (Morris, Kennard, Hall & Smith, 1982)]. The distance for $(CH_3)_3N(SO_3)$ is even longer [1·844 (2) Å (Morris, Kennard, Hall, Smith & White, 1983)]. It is longer than that found for the corresponding potassium salt, $K[CH_3NH(SO_3)]$ [1·637 (4) Å (Morris, Kennard, Hall & Smith, 1982)]. Another interesting trend is that the N—S—O angle [102·4 (7)°] is smaller in the acid than in the potassium salt [106·2 (4)°]. This is a general feature when comparing the acid to its equivalent potassium salt. Another indicator is the S—N—C angle [acid, 113·4 (9)°; potassium salt, 116·4 (3)°].

Extensive intermolecular hydrogen bonding extends the acid into a three-dimensional polymer through HN(2) and O(2) [$\frac{1}{2}+x$, $\frac{1}{2}+z$, $-\frac{1}{2}+y$, N···O 3·10 (1), H···O 2·85 (15) Å, N—H···O 100 (2)°] and bifurcated bonds involving HN(1) and O(2) [$\frac{1}{2}+x$, $\frac{1}{2}+z$, $-\frac{1}{2}+y$, N···O(2) 3·10 (1), H···O 2·59 (14) Å, N—H···O(2) 124 (2)°] and O(3) [$\frac{1}{2}+z$, $\frac{1}{2}+y$, $\frac{1}{2}+x$, N···O(3) 2·81 (1), H···O(3) 2·11 (14) Å, N—H···O(3) 150 (2)°]. The packing diagram is shown in Fig. 2.

The authors wish to thank the Australian Research Grants Committee, the University of Queensland for financial support and the University of Western Australia for use of their diffractometer. One of us (GS) wishes to thank the Queensland Institute of Technology for leave to work on this project.

References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Morris, A. J., Kennard, C. H. L., Hall, J. R. & Smith, G. (1982). *Inorg. Chim. Acta*, **62**, 247–252.
Morris, A. J., Kennard, C. H. L., Hall, J. R., Smith, G. & White, A. H. (1983). *Acta Cryst.* C**39**, 81–82.
Sass, R. L. (1960). *Acta Cryst.* **13**, 320–324.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.