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Molecular Structure and Centrifugal Distortion in Methylthioethyne[1]

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The investigation of the microwave spectra of five isotopic species of methylthioethyne, HC ≡ CSCH$_3$ enabled a fairly reliable calculation to be made of bond lengths and angles. The centrifugal distortion parameters are related to molecular vibrations.

The analysis of the microwave spectra of methylthioethyne, HC≡CSCH$_3$, and the isotopically labelled compound HC≡C^{34}SCH$_3$ was presented in a previous paper (*1*). No reliable bond lengths and angles could be derived from the principal moments of inertia of these two isotopic species. A better structural model of methylthioethyne can now be represented after the completion of the investigation of the microwave spectra of the molecules: DC≡CSCH$_3$, HC≡CS^{13}CH$_3$ and HC≡CSCDH$_2$[3]. Centrifugal distortion constants were deduced from the differences between the accurately measured frequencies of the rotational transitions (in the vibrational ground state) and the corresponding theoretical rigid rotor values (*1*, *2*). The parameters obtained in this way agree favorably with the centrifugal distortion constants evaluated from the data of a normal coordinate analysis of the infrared spectrum of methylthioethyne.

EXPERIMENTAL

The preparation of HC≡CSCH$_3$ has been described previously (*3*, *1*). Therefore we may restrict this discussion to the synthesis of DC≡CSCH$_3$ and HC≡CS^{13}CH$_3$.

A quantity of 3 g DC≡CSCH$_3$ was obtained from 4 g HC≡CSCH$_3$ by exchanging the (acid) acetylenic hydrogen atom for deuterium in a weekly alkaline

[1] Part of a thesis, Utrecht (1968); obtainable upon request.

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[3] The microwave spectra of the two rotational isomers of HC≡CSCDH$_2$ (deuterium in or out of the molecular symmetry plane, called respectively sym- or asym-HC≡CSCDH$_2$), have been studied recently by Dr. G. Ruitenberg. I am very grateful to him for communicating the rotational constants and centrifugal parameters of these compounds.

excess D_2O (99.9% D, Norsk Hydro) (*4*). A deuteration of approximately 95% was reached by repeating this procedure four times.

The methyl group of $HC{\equiv}CSCH_3$ was labelled with ^{13}C according to a reaction scheme of Brandsma *et al.* (*3*):

$$HC{\equiv}CH \xrightarrow{NaNH_2} NaC{\equiv}CH \xrightarrow{S_8} NaSC{\equiv}CH \xrightarrow{CH_3X} CH_3SC{\equiv}CH$$

in which X stands for Br or I.

All these reactions were performed in liquid ammonia. Sodium acetylide was prepared from acetylene by the well known titration method; $NaC{\equiv}CH$ was converted into the thiolate $NaSC{\equiv}CH$ by adding powdered sulphur to the reaction vessel. The methylation of this sulphur compound determined the yield of the synthesis because of the competitive reaction of the solvent—ammonia—with methyl halide. It was found that methyl bromide gave the highest yield (20–25%) with respect to the methyl halide at a temperature of about −65°C.[4]

Treating 3 g methanol (54% ^{13}C, Volk Radio Chemical Comp.) with PBr_3 gave $^{13}CH_3Br$. We got 0.95 g $HC{\equiv}CS\ ^{13}CH_3$, which was a yield of 18% with respect to $^{13}CH_3Br$. From this rather impure quantity of $HC{\equiv}CS\ ^{13}CH_3$ we isolated highly pure samples with a gas chromatograph (F. and M. gas chromatograph, model 720, preparative column of 180-cm length and 0.63-cm diameter containing a stationary phase of 20% di-iso decyl phthalate, H_2 flow 40 ml/min, temperature 80°C).

The microwave spectra were recorded between 17 and 40 GHz with a 10 kHz Stark modulated spectrometer. The stabilization of the klystron frequency and the procedure for measuring the Stark splitting coefficients were described previously (*5*).

Spectra and Constants

The main difference between the microwave spectra of the parent molecule (compound with the most abundant isotopes) of methylthioethyne $HC{\equiv}CSCH_3$ and the isotopic species $DC{\equiv}CSCH_3$ and $HC{\equiv}CS^{13}CH_3$, is a shift of the rotational transitions. For that reason the interpretation of the microwave spectra of the latter compounds was straightforward. The experimental and calculated frequencies of the observed rotational transitions of $DC{\equiv}CSCH_3$ and $HC{\equiv}CS^{13}CH_3$ can be found in Tables I and II, respectively.

The rotational and centrifugal distortion constants were fitted to the measured frequencies by a first order method given by Sørensen (*6*). This author has shown that for an almost planar molecule, dimethylsulphide, the centrifugal distortion up to first order can be described by four parameters. Calculations showed that the same holds for methylthioethyne (Ray's asymmetry parameter κ being −0.883). The constants obtained from the microwave spectra can be found in

[4] I am very indebted to Dr. H. Olsman for helping me with these syntheses.

TABLE I

MICROWAVE ABSORPTION LINES OF $DC{\equiv}CSCH_3$ (MHz)

Transition		Frequency[a]	Delta[b]	Centr. corr.
0 0 0	1 1 1	18 794.050	−0.039	−0.154
1 0 1	2 1 2	24 906.350	0.096	−0.147
2 1 2	2 2 1	38 042.900	−0.134	−2.447
2 1 1	2 2 0	36 104.320	−0.128	−2.370
2 0 2	3 0 3	20 197.900	0.077	−0.159
2 0 2	3 1 3	30 701.500	−0.015	−0.159
2 1 2	3 1 3	19 303.600	0.004	−0.061
2 1 1	3 1 2	21 267.430	0.043	−0.218
2 2 1	3 2 2	20 301.940	−0.031	−0.046
2 2 0	3 2 1	20 405.750	−0.047	−0.070
3 1 3	3 2 2	39 041.040	0.030	−2.432
3 0 3	4 0 4	26 811.110	0.020	−0.360
3 0 3	4 1 4	36 212.550	0.096	−0.194
3 1 3	4 1 4	25 709.150	−0.011	−0.195
3 1 2	4 1 3	28 324.750	−0.250	−0.521
3 2 2	4 2 3	27 048.830	−0.033	−0.229
3 2 1	4 2 2	27 306.410	0.078	−0.308
4 1 3	4 2 2	34 224.380	0.031	−2.009
4 0 4	5 0 5	33 327.460	0.016	−0.657
4 1 4	5 0 5	23 925.900	0.060	−0.823
4 2 3	5 2 4	33 778.170	0.050	−0.550
4 2 2	5 2 3	34 286.430	−0.058	−0.751
5 0 5	5 1 4	17 969.800	0.077	−0.751
5 1 4	5 2 3	33 158.720	0.048	−1.750
5 0 5	6 0 6	39 734.300	−0.071	−1.049
5 1 5	6 0 6	31 568.440	0.056	−1.453
5 1 5	6 1 6	38 447.750	0.012	−0.751
6 0 6	6 1 5	20 575.830	−0.015	−1.420
6 1 5	6 2 4	32 172.050	0.168	−1.505
6 1 6	7 0 7	39 151.090	−0.007	−2.231
7 0 7	7 1 6	23 823.030	−0.064	−2.560
7 1 6	7 2 5	31 399.250	0.063	−1.383
8 0 8	8 1 7	27 745.700	−0.042	−4.331
8 1 7	8 2 6	30 970.600	−0.025	−1.548
9 0 9	9 1 8	32 340.480	0.139	−6.869
9 1 8	9 2 7	31 003.070	−0.028	−2.214
10 1 9	10 2 8	31 596.250	−0.007	−3.643
11 1 10	11 2 9	32 833.190	−0.111	−6.142
11 3 9	12 2 10	33 125.000	−0.013	−15.476
12 1 11	12 2 10	34 781.810	−0.015	−10.062
13 1 12	13 2 11	37 494.980	0.052	−15.761

[a] Experimental uncertainty about 0.05 MHz.

[b] Observed minus calculated frequency.

TABLE II

MICROWAVE ABSORPTION LINES OF HC≡CS $^{13}CH_3$ (MHz)

Transition		Frequency	Delta	Centr. corr.
0 0 0	1 1 1	18 731.550	−0.020	−0.155
1 0 1	2 1 2	25 125.990	0.042	−0.135
2 1 1	2 2 0	34 833.420	−0.060	−2.413
2 1 2	2 2 1	37 009.100	0.029	−2.480
2 0 2	3 0 3	21 257.650	−0.001	−0.186
2 0 2	3 1 3	31 165.400	0.031	−0.126
2 1 2	3 1 3	20 267.550	−0.013	−0.049
2 1 1	3 1 2	22 476.300	−0.100	−0.217
3 1 2	3 2 1	33 885.900	−0.019	−2.157
3 1 3	3 2 2	38 134.830	0.086	−2.364
3 0 3	4 0 4	28 188.480	−0.029	−0.412
3 0 3	4 1 4	36.893.650	−0.025	−0.130
3 1 3	4 1 4	26 985.850	−0.007	−0.190
3 1 2	4 1 3	29 925.970	0.038	−0.563
3 2 2	4 2 3	28 497.930	−0.134	−0.108
3 2 1	4 2 2	28 833.050	0.106	−0.205
4 1 3	4 2 2	32 793.100	−0.071	−1.799
4 1 4	4 2 3	39 646.800	0.070	−2.282
4 0 4	5 0 5	34 996.140	−0.126	−0.737
4 1 4	5 0 5	26 290.810	0.030	−1.019
4 1 4	5 1 5	33 674.700	0.098	−0.428
4 1 3	5 1 4	37 336.600	0.009	−1.129
4 2 3	5 2 4	35 579.430	0.069	−0.442
5 0 5	5 1 4	18 404.300	0.037	−0.723
5 1 4	5 2 3	31 694.100	0.048	−1.374
5 1 5	6 0 6	34 284.640	−0.033	−1.735
6 0 6	6 1 5	21 430.200	0.029	−1.524
6 1 5	6 2 4	30 748.000	−0.042	−0.980
7 0 7	7 1 6	25 201.790	−0.085	−2.934
7 1 6	7 2 5	30 116.860	−0.063	−0.783
8 0 8	8 1 7	29 737.150	−0.036	−5.137
8 1 7	8 2 6	29 950.950	0.007	−1.020
9 0 9	9 1 8	35 000.870	0.001	−8.256
9 1 8	9 2 7	30 379.250	0.065	−1.995
9 3 7	10 2 8	21 278.300	0.027	−7.836
10 1 9	10 2 8	31 508.300	−0.030	−4.071
11 1 10	11 2 9	33 424.650	−0.083	−7.670
12 1 11	12 2 10	36 195.100	0.084	−13.239
13 1 12	13 2 11	39 860.580	−0.039	−21.171
13 4 10	14 3 11	25 903.250	0.010	−22.284

Table III. For the sake of completeness all the investigated isotopic species of methylthioethyne have been inserted in this Table.

The centrifugal distortion parameters $\tau_{\alpha\beta\gamma\delta}$ of Table III can be related to the molecular vibrations (7), namely

TABLE III

ROTATIONAL CONSTANTS (MHz), PRINCIPAL MOMENTS OF INERTIA (amu. Å²) AND CENTRIFUGAL DISTORTION CONSTANTS (kHz) OF SOME ISOTOPIC SPECIES OF METHYLTHIOETHYNE

	HC ≡ $CSCH_3$[a]	DC ≡ $CSCH_3$	HC ≡ $C^{34}SCH_3$[a]	HC ≡ $CS^{13}CH_3$	sym-HC ≡ $CSCDH_2$[d]	asym-HC ≡ $CSCDH_2$[d]
A[b]	15955.18 ± 0.01	15737.95 ± 0.03	15592.0 ± 0.1	15534.44 ± 0.02	15736.23 ± 0.04	14562.16 ± 0.04
B	4002.760 ± 0.004	3711.105 ± 0.003	3982.91 ± 0.03	3933.845 ± 0.003	3809.064 ± 0.008	3930.715 ± 0.008
C	3260.662 ± 0.004	3056.214 ± 0.004	3232.11 ± 0.03	3197.241 ± 0.004	3123.160 ± 0.007	3180.630 ± 0.007
I_a[c]	31.6844	32.1222	32.4224	32.5431	32.1253	34.715
I_b	126.295	136.222	126.925	128.510	132.718	128.610
I_c	155.037	165.409	156.409	158.114	161.865	158.941
τ_{aaaa}	−719 ± 9	−652 ± 23	−380 ± 150	−667 ± 15	−740 ± 12	−530 ± 10
τ_{bbbb}	−14.1 ± 0.2	−11.1 ± 0.2	−13.5 ± 3	−13.5 ± 0.3	−12.3 ± 0.2	−14.1 ± 0.2
τ_{cccc}	−3.1 ± 0.2	−2.7 ± 0.2	−3.9 ± 2.6	−2.6 ± 0.2	−2.8 ± 0.2	−3.2 ± 0.2
τ_{abab}	−40 ± 2	−39 ± 1	—	−38 ± 1	−31.2 ± 0.6	−34.7 ± 0.7

[a] Ref. 1.

[b] Rotational constants calculated from the transitions of the A-type symmetry.

[c] Conversion factor between rotational constants and moments of inertia is 505531 MHz amu Å².

[d] See Footnote [3].

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2I_{\alpha\alpha}I_{\beta\beta}I_{\gamma\gamma}I_{\delta\delta}} \sum_{ij} I_{\alpha\beta}^{(i)} I_{\gamma\delta}^{(j)} (f^{-1})_{ij}, \qquad (1)$$

where $I_{\alpha\beta}$ etc. are the elements of the inertia tensor and each of the subscripts α, β, γ, δ denote one of the principal axes a, b or c; $I_{\alpha\beta}^{(i)}$ is a short notation for $\partial I_{\alpha\beta}^{(i)}/\partial S_i$ where S_i is the ith vibrational symmetry coordinate; $(f^{-1})_{ij}$ is the element ij of the inverted matrix of the force constants on the basis S_i (*8*). The diagonal elements and a few nondiagonal elements of the matrix of force constants have been fitted to the observed infrared frequencies of the normal modes of vibration of HC≡CSCH$_3$ and DC≡CSCH$_3$ (*9*, *10*). However, the normal coordinate analysis was performed with a simplified model in which the methyl group was presented by a point mass 15. It is clear that this model does not account for the methyl group vibrations. The neglect of methyl vibrations (i.e. no appropriated force constants) with respect to the calculation of the τ's can be illustrated by the linear transformation from symmetry to normal coordinates (*8*):

$$\sum_{ij} I_{\alpha\beta}^{(i)} I_{\gamma\delta}^{(j)} (f^{-1})_{ij} = \sum_{k} I_{\alpha\beta}^{(k)} I_{\gamma\delta}^{(k)} (2\pi\nu_k)^{-2} \qquad (2)$$

in which the index k denotes a normal mode of vibration and ν_k is the corresponding eigenfrequency; $I_{\alpha\beta}^{(k)} = \partial I_{\alpha\beta}/\partial Q_k$. Since the methyl vibrations, except the torsional mode, have relatively high frequencies ($\nu_k \geqq 1000$ cm^{-1}), it follows from eq. (2) that their elimination is not unreasonable. The contribution of the torsional vibration of the methyl group to the constants τ_{aaaa} and τ_{bbbb} (τ_{cccc} and τ_{abab} are independent of this out-of-plane vibration) is assumed to be small too, because only two hydrogen atoms have nonzero c-coordinates (see Fig. 1). The numerical calculations of the τ's in accordance with eq. (1) have been performed with a program written by G. O. Sørensen for the G.I.E.R. computer of the

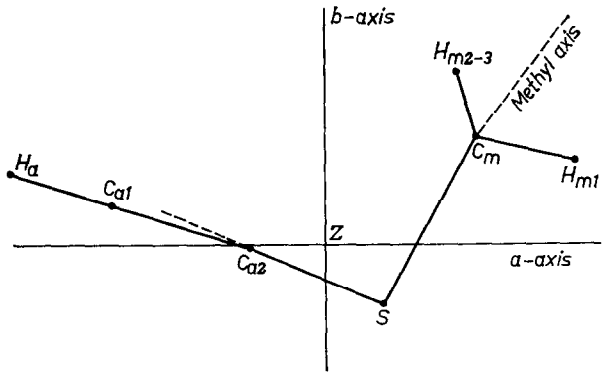

FIG. 1. Z = centre of gravity; c-axis perpendicular to the drawing-plane

University of Copenhagen. The structural data needed for calculating the symmetry coordinates and moments of inertia can be found in Table VI. However, the principal moments of inertia evaluated along these lines were too low by an amount of 2–3%, due to the neglect of the steric extent of the CH_3 group. The centrifugal distortion constants in the column "Infrared" of Table IV, which gives the comparison between infrared and microwave results, have been corrected in this respect.

MOLECULAR STRUCTURE

The following relation between the principal moments of inertia of $HC{\equiv}CSCH_3$ suggests that the molecule belongs to the point group C_s :

$$I_a + I_b - I_c = I_\alpha - \Delta \tag{3}$$

I_α is the moment of inertia of the methyl group about its symmetry axis. Using an approximative procedure reported by Herschbach and Laurie (*11*) we estimated the inertial defect Δ at 0.40 amu. Å^2 by means of our simplified molecular model (methyl group is a point mass) from the infrared frequencies of the low-energy vibrations (<1000 cm^{-1}). Since the A'' vibrations are neglected, the value obtained for Δ is definitely too high.[5] Hence, eq. (3) cannot be used to calculate I_α, from which the distance between the two out-of-plane hydrogen atoms follows.

The coordinates of the atoms H_a, S, C_m, H_{m1}, H_{m2} and H_{m3} (see Fig. 1) of methylthioethyne were obtained from the principal moments of inertia of $HC{\equiv}CSCH_3$, $DC{\equiv}CSCH_3$, $HC{\equiv}C^{34}SCH_3$, $HC{\equiv}CS^{13}CH_3$, sym- $HC{\equiv}CSCDH_2$ and asym- $HC{\equiv}CSCDH_2$ (Table III) using Kraitchman's equations (*12*). Table V shows the result of this calculation. The structural parameters of the SCH_3-group can be derived easily from these coordinates: The sulphur—carbon bond length SC_m is 1.813 Å, the two carbon—hydrogen distances C_mH_{m1} and C_mH_{m2} ($=C_mH_{m3}$) are 1.079 and 1.090 Å, respectively and the three H—C—H angles of the methyl group are 109°51′ (the difference between $\measuredangle H_{m1}C_mH_{m2}$ and $\measuredangle H_{m2}C_mH_{m3}$ is less than 6′).

Although the C_s-symmetry of methylthioethyne does not require equality of the bond lengths C_mH_{m1} and C_mH_{m2}, however, any difference between these distances violates the threefold symmetry of the methyl group. On the other hand, the splitting of the rotational transitions in torsion doublets by the internal rotation of the methyl group is a justification of the assumption of a threefold symmetry axis. From the above we may conclude: Either the calculated deviation from the threefold symmetry is simply an artefact of the substitution method (the nonequilibrium distances of the C_mH_{m1} and C_mH_{m2} bonds are differently affected by the zero-point vibrations), or the doublet splittings are insensible to

[5] The A'' vibrations give rise to a negative contribution to Δ (*11*).

TABLE IV

CENTRIFUGAL DISTORTION CONSTANTS FROM MICROWAVE AND INFRARED SPECTRUM OF METHYLTHIOETHYNE (KHz)[a]

	Microwave	Infrared
τ_{aaaa}	−719	−737
τ_{bbbb}	−14.1	−17.6
τ_{cccc}	−3.1	−3.8
τ_{abab}	−40	−42

[a] The agreement between the τ's from microwave and infrared spectra for the species $DC{\equiv}CSCH_3$ and $HC{\equiv}CS\ ^{13}CH_3$ is as good as for the parent molecule.

distortions of the methyl group (the spacings between the two components of the torsion doublets in methylthioethyne are relatively small (*1*)). Although small deviations from threefold symmetry of the CH_3-group can not be completely ruled out, we prefer the first conclusion, because no appreciable distortion of the symmetry of the methyl group has been detected by studying the internal rotation in similar molecules like $HC{\equiv}COCH_3$ (*15*). Therefore we will stick to the idea of a symmetry axis in the methyl group.

The angle between the methyl (symmetry) axis and the a-axis which has been calculated from the coordinates in Table V, is 57°10′. The corresponding angle between the SC_m bond and the a-axis is found to be 59°27′, from which a "tilt" of 2°20′ follows for the methyl axis. In a previous paper (*1*) we tried to estimate the direction of the methyl axis from the observed spacing between the *A*- and *E*-component of a torsion doublet. The experimental error inherent in the doublet splittings $\nu_A - \nu_E$ did not permit an accurate determination of the angle between the methyl axis and the *a*-axis (56°30′ ± 1°30′ (*1*)). However, both the r_s-coordinates of the methyl group and the internal rotation parameters indicate a "tilt" of the symmetry axis of 2–3° in the direction of the lone electron pairs of the sulphur atom. This kind of distortion of a tetrahedral conformation of XCH_3 groups (X = N, O or S) has been found in many other compounds; for instance the tilt of the methyl axis is 2°37′ in CH_3SCH_3 (*13*); 2°10′ in CH_3SH (*14*); about 5° in $HC{\equiv}COCH_3$ (*15*); 2°30′ in CH_3OCH_3 (*16*) and 5° in CH_3OH (*17*). The significant experimental evidence (mainly from microwave investigations) for the existence of tilted symmetry axes in methyl groups may be related to the potential barrier hindering the free rotation of the internal top. This suggestion was put forward after some calculations of the tilt-dependence of ΔV_{nn}, which is the difference in nuclear repulsion energy between the staggered and eclipsed conformations of the methyl group (*18*) (calculated in methoxyethyne and methylthioethyne). Recently the tilt effect on the potential barrier in methylamine has been estimated by Pedersen and Morokuma (*19*). The results of their "*ab initio*" calculations show that the conformation in which the methyl axis has tilted 3°30′

TABLE V

r_s-COORDINATES OF THE ATOMS H_a, S, C_m, H_{m1} AND H_{m2} IN Å[a]

	a	*b*	*c*
H_a	−3.1552	+0.6990	0
S	+0.5676	−0.6188	0
C_m	+1.4893	+0.9425	0
H_{m1}	+2.5375	+0.6880	0
H_{m2}	+1.2479	+1.5202	+0.8918

[a] Reference is made to Fig. 1.

to the lone pair of electrons of the nitrogen atom is 680 cal/mole more stable than the "classical" structure.

However, the moments of inertia of the five investigated isotopic species of methylthioethyne do not allow a complete determination of the molecular structure. Since the acetylenic carbon atoms C_{a1} and C_{a2} have not been substituted by ^{13}C, *one assumption* has necessarily to be added to the relations (4):

$$\sum_i m_i a_i = 0,$$

$$\sum_i m_i b_i = 0, \qquad (4)$$

$$\sum_i m_i a_i b_i = I_{ab} = 0$$

in order to calculate the coordinates of C_{a1} and C_{a2}. The most logical assumptions which can be made are:

(a) the atoms H_a, C_{a1} and C_{a2} are situated on a straight line;
(b) the atoms C_{a1}, C_{a2} and S are situated on a straight line;
(c) the bond length of H_a C_{a1} is known, for instance 1.060 Å (*20*);
(d) the bond length of C_{a1} C_{a2} is known, for instance 1.210 Å (*20*).

Regarding assumption (b), we found an improbable short distance of the C_{a1} C_{a2} bond, being 1.18 Å, whereas the latter possibilities (c) and (d) were identical with respect to a significant deviation of about 2° from linearity for the angle C_{a1}—C_{a2}—S. Assuming the four atoms H_a, C_{a1}, C_{a2} and S to be on a straight line, it is impossible to satisfy the three equations of (4) simultaneously: this is an indication that the acetylenic part of the molecule has been cocked too. It may be concluded that on the basis of assumption (a) realistic bond lengths and angles can be obtained.

A summary of the bond distances and angles of methylthioethyne is shown in Table VI. Electron diffraction patterns of $HC{\equiv}CSCH_3$ have been studied by van Eijck (*21*). The results of this investigation can also be found in Table VI. It is not self-evident that such basically different methods as microwave spectroscopy and electron diffraction lead to an almost similar molecular structure. The rota-

TABLE VI

MOLECULAR STRUCTURE OF METHYLTHIOETHYNE
COMPARISON WITH THE RESULTS OF ELECTRON DIFFRACTION (*21*)

	Microwave	Electron diff.
H_aC_{a1}	1.061 ± 0.006 Å	[a]
$C_{a1}C_{a2}$	1.205 ± 0.007 Å	1.215 ± 0.003 Å
$C_{a2}S$	1.685 ± 0.005 Å	1.682 ± 0.003 Å
SC_m	1.813 ± 0.002 Å	1.814 ± 0.003 Å
C_mH_{m1}	1.079 ± 0.007 Å	[a]
C_mH_{m2}	1.090 ± 0.005 Å	[a]
$\measuredangle H_{m1}C_mH_{m2}$	109°52′ ± 20′	[a]
$\measuredangle C_mSC_{a2}$	99°55′ ± 10′	100° ± 30′
$\measuredangle C_{a1}C_{a2}S$	182° ± 20′	[a]
$\measuredangle H_aC_{a1}C_{a2}$	180°[b]	[a]
Tilt methyl axis	2-3°	

[a] No reliable values have been derived.
[b] Assumed.

tional constants of $HC{\equiv}CSCDH_2$ indicate a staggered conformation of the methyl group. Evidence for the staggered conformation has also been found by van Eijck (*21*).

The length of the short C—S bond distance in methylthioethyne is about 0.02 Å shorter than the C—S bond in sulphur dicyanide (*22*) and nearly as long as the corresponding C—S bond in methylthiocyanate (*23*). The titled acetylenic structure in $HC{\equiv}CSCH_3$ is a rather unexpected result of our investigations. However, cocked conformations at "sp hybridized" carbon atoms have been observed in sulphur dicyanide (*22*) and in a carbonyl compound (*24*).

DIPOLE MOMENT

The dipole moment of methylthioethyne was derived from the stark splitting measurements on 1.69 D at some rotational transitions of the parent molecule (*1*). The calculation of the second-order Stark splitting of the rotational energy levels requires the knowledge of line strengths (*25*). Interpolation to $\kappa = -0.883$ (the asymmetry parameter of $HC{\equiv}CSCH_3$) from the line strengths tabulated by Schwendeman and Laurie (*26*) is troublesome and in some cases serious errors have been introduced. It was therefore desired to revise the calculation of the dipole moment, having at our disposal accurate line strengths obtained from a rigid rotor program. The new and more reliable value for the dipole moment of methylthioethyne is much lower: 1.59 ± 0.05 D. This number was confirmed after the digestion of the measurements of the Stark effect of $DC{\equiv}CSCH_3$. The Stark displacements of the deutero compound were determined at the rotational transitions 2_{02}–3_{13}, 3_{03}–4_{14} and 4_{04}–5_{05}.

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