Microwave Spectrum, Structure, Dipole Moment, and Barrier to Internal Rotation of Methylthioethyne

D. DEN ENGELSEN

Laboratory of Organic Chemistry, State University of Utrecht, Utrecht, The Netherlands

The microwave absorption spectrum is reported as well as rotational constants, dipole moment components, and centrifugal distortion constants of methylthioethyne. The spectra of two isotopic species of methylthioethyne were measured, namely, $HC\equiv C-{}^{32}SCH_3$ and $HC\equiv C-{}^{34}SCH_3$; the determination of the molecular structure therefore implies some assumptions about certain bond lengths and bond angles. The potential barrier to the internal rotation of the methyl group is derived from the observed doublet splittings.

INTRODUCTION AND EXPERIMENTS

Structure determinations by microwave techniques on methylthioethyne and methoxyethyne were carried out as a contribution to a study of their contrasting chemical behavior (*1*). This paper presents information obtained from the spectra of the thioether. Some results on methoxyethyne have been communicated before (*2*).

Methylthioethyne was prepared treating sodium acetylide with sulfur and methyliodide according to Brandsma *et al.* (*3*).[1] The microwave spectrum of this compound was recorded from 17.3–40.5 GHz with the aid of a conventional Stark spectrograph, details of which have been given elsewhere (*2*). The natural abundance of ${}^{34}S$, namely, 4.2 %, proved to be sufficient to identify a number of absorption lines belonging to the ${}^{34}S$-species. Improvement of the signal to noise ratio of the rotational transitions in the vibrational ground state was obtained by cooling the Stark cell to 220°K. The determination of the Stark splitting coefficients proceeded in essentially the same way as described in Reference *2* by using a stabilized klystron frequency.

MICROWAVE SPECTRUM AND CALCULATION OF CONSTANTS

In the spectrum of methylthioethyne *c*-type transitions are absent, *a*-type lines are weak, and *b*-type lines are relatively strong, whereas methoxyethyne gives rise to *a*- and *b*-type lines of comparable magnitude. This behavior reflects the directions of the dipole moments relative to the principal axes. In methylthio-

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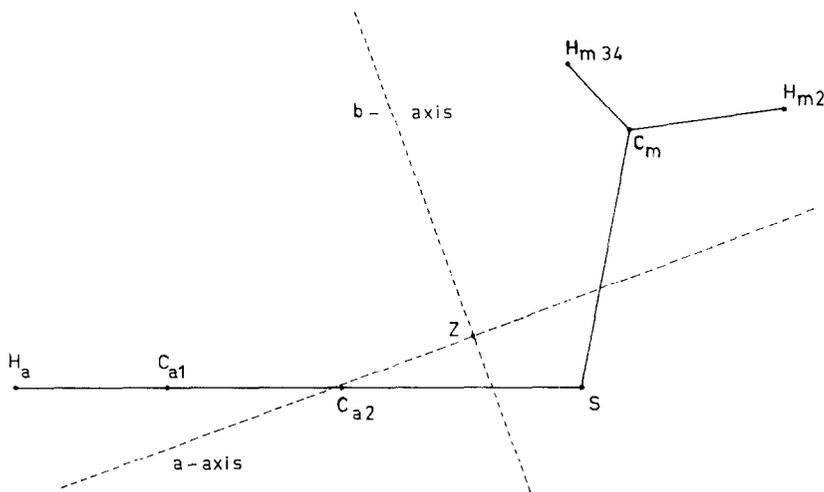[1] The author thanks Dr. L. Brandsma for preparing the sample.

FIG. 1. Molecular model of methylthioethyne. The c-axis is perpendicular to the drawing plane. The inserted Z denotes the center of gravity.

ethyne the dipole moment vector coincides more nearly with the b-axis. A model of the latter molecule is given in Fig. 1.

The threefold barrier, which hinders the rotation of the methylgroup about its symmetry axis, splits the rotational energy levels of an asymmetric molecule into nondegenerate A- and degenerate E-levels. This doublet splitting $\nu_A - \nu_E$ could be observed in the ground state of the torsional vibration for two bQ-transition series of methylthioethyne. The frequency splitting of other transitions appeared too small to be observed ($\nu_A - \nu_E < 200$ kHz).

Correct assignment of rotational transitions of $HC\equiv C-^{32}SCH_3$ could be proved by the Stark effect for some low J-values ($J < 5$); high J-transitions ($J > 5$) were assigned by calculation including in some cases centrifugal distortion corrections. The rotational constants and centrifugal distortion parameters were calculated from the observed transitions according to a least squares method outlined by Sørensen (4). For $HC\equiv C-$ $^{32}SCH_3$) reliable values of the centrifugal distortion constants could be obtained from b-type transitions up to $J = 15$.

The roughly 20 times weaker spectrum of $HC\equiv C-^{34}SCH_3$ could be identified by calculation only.[2] Because of the low intensity of these lines only the strongest could be osberved, and their frequencies contain a greater experimental uncertainty. So the values of the rotational constants and centrifugal distortion parameters are necessarily less accurate.

In the spectrum a satellite bQ-transition series was detected, it is not yet clear

[2] The suggestions of J. Rastrup-Andersen were very valuable for the identification of this weak spectrum.

TABLE   I

Absorption lines of $HC\equiv C-^{32}SCH_3$ (MHz) [a]

transition	observed frequency	calc-obs frequency	centr. dist. correction
$0_{00} - 1_{11}$	19215.63	+0.04	-0.17
$1_{01} - 2_{12}$	25736.93	+0.06	-0.17
$2_{12} - 2_{21}$	38080.70	+0.16	-2.68
$2_{11} - 2_{20}$	35888.21	-0.08	-2.61
$2_{02} - 3_{03}$	21656.50	+0.04	-0.20
$2_{02} - 3_{13}$	31900.15	+0.11	-0.19
$2_{12} - 3_{13}$	20656.50	+0.06	-0.08
$2_{11} - 3_{12}$	22881.70	+0.03	-0.26
$3_{13} - 3_{22}$	39214.55	-0.02	-2.63
$3_{12} - 3_{21}$	34930.22	-0.09	-2.41
$3_{03} - 4_{04}$	28722.35	-0.01	-0.46
$3_{03} - 4_{14}$	37748.73	-0.01	-0.23
$3_{13} - 4_{04}$	18478.50	+0.12	-0.47
$3_{13} - 4_{14}$	27505.00	0.00	-0.25
$3_{12} - 4_{13}$	30467.20	+0.14	-0.64
$4_{13} - 4_{22}$	33821.00	-0.06	-2.12
$4_{04} - 5_{05}$	35666.20	-0.07	-0.82
$4_{14} - 5_{05}$	26639.72	+0.03	-1.05
$4_{14} - 5_{15}$	34324.42	-0.02	-0.53
$4_{13} - 5_{14}$	38014.50	-0.11	-1.26
$4_{23} - 5_{24}$	36242.05	-0.02	-0.66
$4_{41} - 5_{42}$	36391.72	-0.02	+0.17
$4_{40} - 5_{41}$	36391.72	+0.16	+0.17

whether these lines belong to rotational transitions in the first excited torsional state or to another excited vibrational state. The appropriate constants are: $\kappa = -0.8814$ and $\frac{1}{2}(A-C) = 6176.6$ MHz.

The observed frequencies, differences between observed and calculated fre-

TABLE   I   continued.

transition	observed frequency	calc-obs frequency	centr. dist. correction
$5_{05} - 5_{14}$	18788.35	+0.02	-0.85
$5_{14} - 5_{23}$	32698.40	-0.08	-1.77
$5_{15} - 6_{06}$	34791.03	-0.16	-1.81
$6_{06} - 6_{15}$	21822.43	+0.02	-1.71
$6_{15} - 6_{24}$	31719.82	-0.01	-1.45
$6_{25} - 7_{16}$	23467.65	-0.11	-2.81
$7_{07} - 7_{16}$	25604.44	+0.07	-3.18
$7_{16} - 7_{25}$	31047.52	-0.02	-1.32
$7_{26} - 8_{17}$	33165.42	+0.01	-5.49
$8_{08} - 8_{17}$	30156.54	-0.01	-5.48
$8_{17} - 8_{26}$	30832.52	0.00	-1.60
$9_{09} - 9_{18}$	35447.85	-0.04	-8.74
$9_{18} - 9_{27}$	31205.27	+0.04	-2.59
$9_{37} - 10_{28}$	20777.65	-0.03	-6.45
$10_{19} - 10_{28}$	32273.95	-0.03	-4.64
$10_{38} - 11_{29}$	31182.25	+0.03	-13.46
$11_{110} - 11_{29}$	34126.80	+0.04	-8.16
$12_{111} - 12_{210}$	36833.35	-0.03	-13.61
$13_{112} - 13_{211}$	40437.70	-0.03	-21.39
$13_{410} - 14_{311}$	25091.00	-0.11	-17.83
$14_{411} - 15_{312}$	35565.30	+0.10	-33.54

[a] The experimental uncertainty is about 0.05 MHz.

quencies, and the centrifugal distortion corrections for both molecular species are given in Tables I (HC≡C—^{32}SCH$_3$) and II (HC≡C—^{34}SCH$_3$). Table III shows rotational constants, centrifugal distortion constants, and principal moments of inertia.

TABLE II

ABSORPTION LINES OF HC≡C—^{34}SCH$_3$ (MHz)[a]

Transition	Observed frequency	Calc − obs frequency	Centr. dist. correction
1_{01}–2_{12}	25 288.30	−0.02	−0.10
2_{02}–3_{13}	31 390.50	+0.28	−0.14
3_{03}–4_{04}	28 511.75	−0.02	−0.46
3_{03}–4_{14}	37 177.25	−0.14	−0.23
3_{13}–4_{14}	27 290.85	−0.13	−0.29
3_{12}–4_{13}	30 287.40	−0.01	−0.61
4_{14}–5_{05}	26 726.25	+0.01	−1.07
5_{05}–5_{14}	18 559.50	+0.03	−0.65
5_{14}–5_{23}	31 683.75	+0.15	−0.67
5_{15}–6_{06}	34 804.95	+0.04	−1.81
6_{15}–6_{24}	30 740.60	−0.18	−0.44
7_{07}–7_{16}	25 514.75	−0.23	−2.64
7_{16}–7_{25}	30 127.30	+0.06	−0.40
8_{08}–8_{17}	30 151.40	+0.09	−4.59
8_{17}–8_{26}	29 998.30	−0.20	−0.77
9_{09}–9_{18}	35 526.00	+0.04	−7.32
9_{18}–9_{27}	30 483.60	−0.05	−1.79
10_{19}–10_{28}	31 691.15	+0.32	−3.79
12_{111}–12_{210}	36 604.25	−0.10	−12.18

[a] The experimental uncertainty is about 0.15 MHz.

TABLE III

ROTATIONAL CONSTANTS (MHz), PRINCIPAL MOMENTS OF INERTIA (amu Å^2),
AND CENTRIFUGAL DISTORTION CONSTANTS (kHz) OF METHYLTHIOETHYNE

Constant	HC≡C—^{32}SCH$_3$	HC≡C—^{34}SCH$_3$
A	15 955.175 ± 0.016	15 592.04 ± 0.12
B	4002.760 ± 0.004	3982.91 ± 0.03
C	3260.662 ± 0.004	3232.11 ± 0.03
I_a[a]	31.6844	32.4224
I_b[a]	126.295	126.925
I_c[a]	155.037	156.409
T_1[b]	−719 ± 9	−380 ± 150
T_2[b]	−14.1 ± 0.2	−13.5 ± 2.9
T_3[b]	−3.1 ± 0.2	−3.9 ± 2.6
$T_4 + \dfrac{A-B}{A-B} T_6$[b]	−40 ± 2	[c]
$T_5 + \dfrac{B-C}{A-C} T_6$[b]	−0.3 ± 0.1	[c]

[a] The conversion factor between rotational constants and moments of inertia is **505 531** MHz amu Å^2.

[b] Centrifugal distortion constants defined by Sørensen (4).

[c] No reliable values could be obtained.

TABLE IV

STRUCTURAL DATA, DIPOLE MOMENT, AND BARRIER PARAMETERS. COMPARISON
BETWEEN METHYLTHIOETHYNE AND METHYLTHIOCYANATE[a]

	H—C≡C—SCH₃	N≡C—SCH₃
H_a—C_{a1} (Assumed)	1.060 Å	—
C_{a1}—C_{a2} (Assumed)	1.210 Å	—
C_{a2}—S (Calculated)	1.680 Å	1.684 Å
C_m—S (Calculated)	1.815 Å	1.820 Å
C_m—H (Assumed)	1.093 Å	1.093 Å
C_{a2}—S—C_m (Calculated)	101°	99° 52′
H—C—H (Assumed)	109° 28′	109° 28′
Tilt (CH₃-axis) (Estimated)	2°	—
μ_a	1.00 ± 0.03 D	4.03 D
μ_b	1.36 ± 0.005 D	—
μ_t	1.69 ± 0.03 D	4.03 D
I_α (Assumed)	3.186 amu Å	3.212 amu Å
λ_a	0.550	0.513
λ_b	0.835	0.858
F	166.6 GHz	164.94 GHz
V_3	1750 cal/mole	1600 cal/mole
ΔA	0.255 MHz	—
ΔB	0.037 MHz	—

[a] See Reference 6.

TABLE V

OBSERVED AND CALCULATED STARK SPLITTING COEFFICIENTS (MHz·cm²/kV²)

Transition	Observed	Calculated
3_{03}–4_{14} $M = 0$	−4.21	−4.21
$M = ±1$	−2.65	−2.66
$M = ±2$	+2.00	+2.00
$M = ±3$	+9.70	+9.75
2_{02}–3_{13} $M = 0$	−13.1	−13.2
$M = ±1$	−7.27	−7.23
$M = ±2$	+10.5	+10.4
1_{01}–2_{12} $M = ±1$	+10.1	+10.2

MOLECULAR STRUCTURE

The principal moments of inertia obtained from the rotational constants of
HC≡C—³²SCH₃ and HC≡C—³⁴SCH₃ supply insufficient information for a
complete determination of the molecular structure. Therefore a number of as-
sumptions were introduced, namely, a tetrahedral methyl group, in which the
C—H bond lengths are 1.093 Å, a C≡C bond length of 1.210 Å and a length of
1.060 Å for the neighboring C—H bond (see Fig. 1). On this basis the lengths of

both C—S bonds and the angle between these bonds were fitted to the experimental moments of inertia. Calculations have shown that a deviation from a tetrahedral methyl group, namely, the "tilt" of the axis of the methyl group, estimated at 2° (see below), is negligible since it hardly influences the adjustment of the molecular structure. The general occurrence of a methyl axis "tilted" or "cocked" to the lone pair(s) of O, S, or N atoms has been discussed by Pierce and Hayashi (5).

The structural data are summarized in Table IV. For comparison the corresponding parameters for methylthiocyanate (6) are given in the last column. As could be expected the C—S—C bond angle is about 12° smaller than the C—O—C angle in methoxyethyne (2).

DIPOLE MOMENT

The dipole moment was derived from the Stark displacements of three b-type transitions: 1_{01}–2_{12}, 2_{02}–3_{13}, and 3_{03}–4_{14}. The frequency displacement of the Stark components was followed over a range of the electric field strength from 0 to about 2000 V/cm. Within this range the Stark effect appeared to be quadratic. For the 1_{01}–2_{12} transition only the $M = \pm 1$ Stark component showed a quadratic Stark effect. The theoretical second-order Stark splitting coefficients were calculated according to Golden and Wilson (7) from transition frequencies, and line strengths tabulated by Schwendeman and Laurie (8).

The dipole moment μ_t and its components μ_a and μ_b are given in Table IV and the values of the measured and the calculated Stark splitting coefficients are listed in Table V. Since the contribution of μ_a^2 to the Stark splitting coefficients is relatively small, the uncertainty in μ_a is rather large and estimated to be 0.03 D.

The dipole moments of several acetylenic ethers and thioethers have been determined by Drenth et al. (9, 10) by measuring the dielectric constants of their benzene solutions. However, since this method differs basically from the microwave method, the results from the two techniques are hard to compare.

BARRIER TO INTERNAL ROTATION

The A-E splitting of the rotational energy levels at relatively high potential barriers can be approximated with the principal axis method (P.A.M.), according to Lin and Swalen (11) by considering only second-order perturbation terms:

$$\Delta W_{A\text{-}E} = (\delta W/\delta A)\Delta A + (\delta W/\delta B)\Delta B + (\delta W/\delta A)\Delta C. \tag{1}$$

Differentiation of the energy expression of the rigid asymmetric rotor with respect to the corresponding rotational constants gives $\delta W/\delta A$, etc. Following Herschbach (12) ΔA can be written

$$\Delta A = \alpha^2 F(w_{0A}^{(2)} - w_{0E}^{(2)}). \tag{2}$$

Corresponding expressions apply to ΔB and ΔC by changing α by β and γ, respectively. The structural parameters α, β, γ, and F are dependent on the moment of inertia of the internal rotor I_α about its symmetry axis, the direction cosines λ_a, λ_b, and λ_c of this symmetry axis with respect to the principal axes, and the principal moments of inertia (see Reference *12*). The second-order perturbation coefficients $w_{OA}^{(2)}$ and $w_{OE}^{(2)}$ of Eq. (2) have been tabulated by Herschbach (*12*) as a function of the barrier height V_3 divided by F.

In methylthioethyne the symmetry axis of the methyl group is at right angles to the c-axis; hence the direction cosine $\lambda_c = 0$ and $\Delta C = 0$. Equation (1) was applied in order to calculate the barrier parameters ΔA and ΔB from the well-resolved doublet splittings of two bQ-transition series. Assuming that these values are sufficiently reliable, the ratio of the structural parameters α and β can be found from Eq. (2) (dividing of ΔA by ΔB) and from this result the direction cosines λ_a and λ_b can be found, since $\lambda_a^2 + \lambda_b^2 = 1$. In view of the uncertainty in the observed line splittings the "tilt" of the methyl-group axis could not be determined within $1°$.

The values for ΔA, ΔB, I_α, λ_a, λ_b, F, and V_3 are given in Table IV. Table VI shows a comparison between observed and calculated line splittings $\nu_A - \nu_E$.

The barrier of methylthioethyne $V_3 = 1750$ cal/mole is roughly 300 cal/mole higher than the barrier to internal rotation of methoxyethyne, which is reasonable in view of the larger bond angle C—O—C in the latter compound. The reason why the barrier reported for methylthiocyanate [1600 cal/mole (*6*)] is definitely lower, is not clear.

TABLE VI

CALCULATED AND OBSERVED DOUBLET SPLITTINGS $\nu_A - \nu_E$ (MHz)

Transition	Observed	Calculated
$5_{05}-5_{14}$	0.69 ± 0.05	0.59
$6_{06}-6_{15}$	0.76 ± 0.05	0.76
$7_{07}-7_{16}$	0.95 ± 0.05	0.97
$8_{08}-8_{17}$	1.26 ± 0.05	1.22
$9_{09}-9_{18}$	1.53 ± 0.05	1.50
$5_{14}\ 5_{23}$	0.55 ± 0.05	0.54
$6_{15}-6_{24}$	0.53 ± 0.05	0.52
$7_{16}-7_{25}$	0.54 ± 0.05	0.54
$8_{17}-8_{26}$	0.53 ± 0.05	0.59
$9_{18}-9_{27}$	0.65 ± 0.05	0.70
$10_{19}-10_{28}$	0.84 ± 0.05	0.85
$11_{110}-11_{29}$	1.03 ± 0.05	1.05
$12_{111}-12_{210}$	1.29 ± 0.05	1.30
$13_{112}-13_{211}$	1.57 ± 0.05	1.61

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