# Molecular Structures of 5-Thiabicyclo[2.1.1]hexane and 7-Thianorbornane as Studied by Gas Electron Diffraction

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Molecular structures of 5-thiabicyclo[2.1.1]hexane and 7-thianorbornane (7-thiabicyclo[2.2.1]heptane) were studied by gas electron diffraction. For 7-thianorbornane the rotational constants obtained by Hirota *et al.* by microwave spectroscopy were also taken into account. Least-squares analyses gave the following $r_g$ bond distances and valence angles ($r_\alpha$ for 5-thiabicyclo[2.1.1]hexane and $r_{av}$ for 7-thianorbornane): for 5-thiabicyclo[2.1.1]hexane, $(C_1\text{–}C_2,\ C_2\text{–}C_3)_{av}=1.539\pm0.016$ Å, $C_1\text{–}C_6=1.564\pm0.024$ Å, $C\text{–}S=1.865\pm0.004$ Å, $(C\text{–}H)_{av}=1.110\pm0.008$ Å, $\angle C\text{–}S\text{–}C=69.5\pm0.6°$ and the dihedral angles $(C_1SC_4)\text{-}(C_1C_2C_3C_4)=115.2\pm1.7°$ and $(C_1C_6C_4)\text{-}(C_1C_2C_3C_4)=116.1\pm2.4°$; for 7-thianorbornane, $C_1\text{–}C_2=1.538\pm0.006$ Å, $C_2\text{–}C_3=1.561\pm0.015$ Å, $C\text{–}S=1.837\pm0.004$ Å, $(C\text{–}H)_{av}=1.115\pm0.008$ Å, $\angle C\text{–}S\text{–}C=80.2\pm0.8°$, the dihedral angle $(C_1C_2C_3C_4)\text{-}(C_4C_5C_6C_1)=115.0\pm1.2°$ and $\angle H\text{–}C\text{–}H=106\pm5°$. The uncertainties represent the estimated limits of experimental error. The C–S bond length in 5-thiabicyclo[2.1.1]hexane is longer than that in dimethyl sulfide by 0.06 Å and that in 7-thianorbornane by 0.03 Å. The C–S–C angle in 5-thiabicyclo[2.1.1]hexane is smaller than that in dimethyl sulfide by about 30° and that in 7-thianorbornane by about 11°. The $C_1\text{–}C_6$ bond in 5-thiabicyclo[2.1.1]hexane is longer than the weighted average of the $C_1\text{–}C_2$ and $C_2\text{–}C_3$ bond lengths. The $C_1\text{–}C_2$ bond in 7-thianorbornane is longer than the $C_2\text{–}C_3$ bond.

Bicyclic compounds provide important clues for understanding the relationship between the geometry of molecules and intramolecular forces, since their bond lengths and angles are often very different from the corresponding values in open-chain molecules. When a heteroatom is introduced into a bicyclic system, the system is further distorted. As one of such systems, the structure of 7-oxanorbornane[1] was recently studied. The present paper is concerned with the structures of two thiabicyclic compounds, 5-thiabicyclo[2.1.1]hexane (TBH) and 7-thianorbornane (TN) (Fig. 1). After our preliminary report on their structures[2] was published, a further refinement was made, particularly for the latter molecule, since a set of rotational constants for TN became available.[3] By means of a joint analysis of electron diffraction and spectroscopic data the two non-equivalent C–C distances, $C_1\text{–}C_2$ and $C_2\text{–}C_3$ have been determined independently.

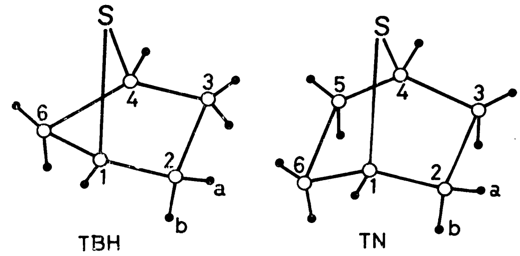


Fig. 1. 5-Thiabicyclo[2.1.1]hexane (TBH) and 7-thianorbornane (TN).

## Experimental

The samples were prepared by the procedures described in the literature[4] and were purified by sublimation and recrystallization. By using a high-temperature nozzle[5] the samples were vaporized at about 60 °C (TBH) and 105 °C (TN), and diffraction photographs were taken with nozzle-to-plate distances of about 249.07 and 114.39 mm. The accelerating voltage of the electrons, about 40 kV, was stabilized within ±0.01% during the experiment.

The scale factors of the diffraction patterns taken with the short camera length were calibrated with reference to the $r_a$(C=O) distance[6] of carbon dioxide measured under essentially the same experimental conditions as those for the sample gases. In the experiment with the long camera length, nitrogen was used as a reference gas. Other experimental details are described in Refs. 6 and 7.

Three photographic plates taken with each camera length were selected for the analysis, and their optical densities were measured by means of a microphotometer and an integrating digital voltmeter.[8] After correction for imperfection in the $r^3$-sector and drawing smooth background curves,[7] molecular scattering intensities were obtained in the ranges $s=2.8\text{—}20.1$ Å$^{-1}$ and $s=7.9\text{—}34.6$ Å$^{-1}$ from the long distance and the short distance data, respectively, at intervals of $s=$

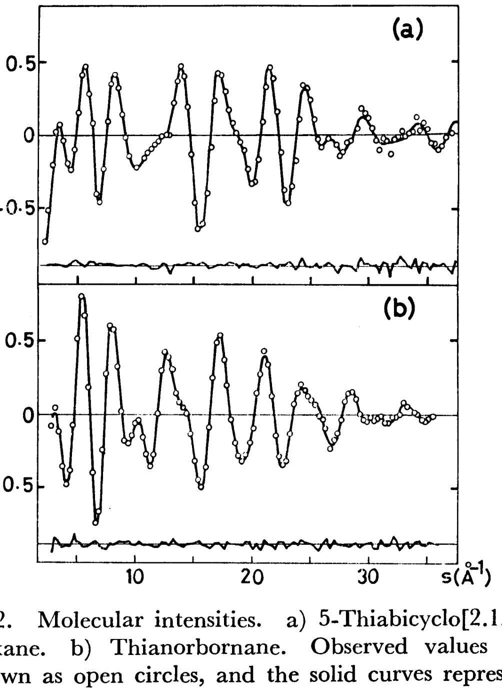


Fig. 2. Molecular intensities. a) 5-Thiabicyclo[2.1.1]hexane. b) Thianorbornane. Observed values are shown as open circles, and the solid curves represent the best-fit theoretical intensities. The lower solid curves represent the residuals.

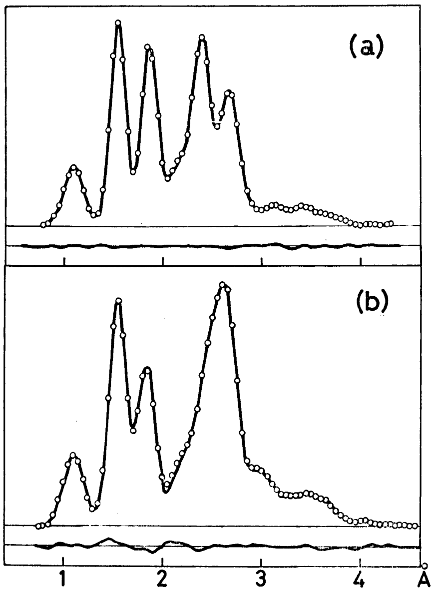


Fig. 3. Experimental (open circles) and the theoretical radial distribution curves. a) 5-Thiabicyclo[2.1.1]-hexane. b) 7-Thianorbornane. Damping factors, $\exp(-0.0016s^2)$ for a) and $\exp(-0.0018s^2)$ for b), were used. The residuals are shown below in the same scale.

$\pi/10$. Since the intensities from the two camera lengths agreed in their overlapping region, they were joined at $s=11.9$ Å$^{-1}$. The elastic and inelastic scattering factors and the phase shifts used for correction of the non-nuclear scattering were taken from the tables prepared by Schäfer *et al.*[9] Typical molecular intensity curves are shown in Fig. 2,[10] and the corresponding radial distribution curves are shown in Fig. 3. Most of the calculations were carried out on a HITAC 8800/8700 in the Computer Center of the University of Tokyo.

## Analysis

*Analysis of Electron Diffraction Data.* The molecular intensities were analyzed by a least-squares method. In order to limit the variable parameters to a tractable number, the following assumptions were made.

1) TBH and TN have $C_s$ and $C_{2v}$ symmetry, respectively.

2) The H–C–H plane in the methylene group is perpendicular to the C–C–C plane, and bisectors of the C–C–C angle and the H–C–H angle are colinear.

3) The C–C–H angles and the S–C–H angle at the bridgehead are equal to one another, *i.e.*, $\angle C_2\text{–}C_1\text{–}H = \angle S\text{–}C_1\text{–}H = \angle C_6\text{–}C_1\text{–}H$.

4) All the C–H bond lengths are equal.

5) All the H–C–H bond angles are equal. For TBH the angles are assumed to be 110° and are not varied in the analysis.

6) The $C_1$–$C_2$ and $C_2$–$C_3$ bond lengths are equal. With these assumptions, the structure of TBH is defined by seven parameters: the weighted average of $C_1$–$C_2$ and $C_2$–$C_3$ bond lengths, the $C_1$–$C_6$, and C–S bond lengths, the weighted average C–H bond lengths, the C–S–C angle and the two dihedral angles: $\angle(C_1SC_4)$-$(C_1C_2C_3C_4)$ and $\angle(C_1C_6C_4)$-$(C_1C_2C_3C_4)$. TN For the following six parameters are taken as variables: the weighted average C–C and C–H bond lengths, C–S–C and the weighted average H–C–H angles, and the dihedral angle $\angle(C_1C_2C_3C_4)$-$(C_4C_5C_6C_1)$. In the analysis of the TN structure the last assumption 6) was released by the joint use of diffraction and spectroscopic data, whereas the other constraints were maintained throughout.

Table 1. Estimated force constants for 5-thiabicyclo[2.1.1]hexane and 7-thianorbornane[a)]

| | | | | | |
|---|---|---|---|---|---|
| *K*(C–C) | 2.30 | *H*(S–C–C) | 0.07 | *F*(S–C–C) | 0.70 |
| *K*(C–S) | 1.75 | *H*(C–C–C) | 0.32 | *F*(C–C–C) | 0.20 |
| *K*(C–H) | 4.25 | *H*(C–S–C) | 0.24 | *F*(C–S–C) | 0.21 |
| *Y*(C–C)$_g$ | 0.15[b)] | *H*(S–C–H) | 0.17 | *F*(S–C–H) | 0.39 |
| *Y*(C–C)$_c$ | 0.11[b)] | *H*(C–C–H) | 0.21 | *F*(C–C–H) | 0.47 |
| *Y*(C–S) | 0.05 | *H*(H–C–H) | 0.40 | *F*(H–C–H) | 0.18 |

a) Estimated force constants taken from cyclohexane[11] and ethyl methyl sulfide.[12] The torsional force constants (*Y*) are in mdyn·Å and the others are in mdyn/Å units. b) Symbols g and c represent the C–C axes which have *gauche* and *cis* C···C atom pairs, respectively.

In addition to the geometrical parameters, a number of mean amplitudes were determined by the least-squares analysis: the average C–H, bonded C–S and nonbonded $C_2$–S and $C_6$–S amplitudes for TBH, and the average C–C, C–H amplitudes, bonded C–S and nonbonded $C_2$–S amplitudes for TN. The rest of the mean amplitudes were fixed to values calculated by the use of Urey-Bradley force constants. Since the vibrational spectra of TBH and TN have not been observed, the force constants transferred from cyclohexane[11] and ethyl methyl sulfide[12] were used without further refinement. They are given in Table 1. In order to apply assumption 1), corrections for the shrinkage effects, $r_a-r_\alpha$,[13,14] were also calculated on the basis of this force field for all the internuclear distances. The calculated mean amplitudes and the shrinkage corrections are shown in Tables 2 and 3. The asymmetry parameter $\kappa$ for the C–H bond was estimated to be $1.2\times10^{-5}$ Å$^3$ by a diatomic approximation.[15] The $\kappa$ parameters for the other atom pairs were assumed to be zero.

Table 2. Mean amplitudes ($l_{ij}$) and shrinkage corrections ($r_a-r_\alpha$) for 5-thiabicyclo-[2.1.1]hexane[a)] (in $10^{-4}$ Å)

| | $l_{ij}$ | $r_a-r_\alpha$ | | $l_{ij}$ | $r_a-r_\alpha$ |
|---|---|---|---|---|---|
| $C_1$–$C_2$ | 529 | 15 | $C_2\cdots H_1$ | 1014 | 33 |
| $C_2$–$C_3$ | 526 | 25 | $C_2\cdots H_3$ | 1059 | 128 |
| $C_1$–$C_6$ | 534 | 8 | $C_2\cdots H_4$ | 958 | 19 |
| $C_1$–S | 549 | 0 | $C_2\cdots H_{6a}$ | 1017 | 27 |
| C–H | 777 | 86 | $C_2\cdots H_{6b}$ | 1468 | −20 |
| $C_1\cdots C_3$ | 613 | 0 | $C_6\cdots H_1$ | 1029 | 25 |
| $C_1\cdots C_4$ | 588 | 1 | $C_6\cdots H_{2a}$ | 1202 | 56 |
| $C_2\cdots C_6$ | 727 | −5 | $C_6\cdots H_{2b}$ | 2029 | −62 |
| $C_2\cdots S$ | 686 | −8 | $S\cdots H_1$ | 1058 | 14 |
| $C_6\cdots S$ | 574 | −1 | $S\cdots H_{2a}$ | 2143 | −91 |
| $C_1\cdots H_2$ | 1420 | 63 | $S\cdots H_{2b}$ | 1125 | 53 |
| $C_1\cdots H_6$ | 1049 | 37 | $S\cdots H_{6a}$ | 1331 | −8 |
| $C_1\cdots H_3$ | 1383 | 36 | $S\cdots H_{6b}$ | 916 | 31 |
| $C_1\cdots H_4$ | 935 | 23 | $H_{2a}\cdots H_{2b}$ | 1246 | 364 |

a) Calculated at 60 °C.

TABLE 3. MEAN AMPLITUDES ($l_{ij}$) AND SHRINKAGE CORRECTIONS ($r_a-r_\alpha$) FOR 7-THIANORBORNANE[a)] (in $10^{-4}$ Å)

| | $l_{ij}$ | $r_a-r_\alpha$ | | $l_{ij}$ | $r_a-r_\alpha$ |
|---|---|---|---|---|---|
| $C_1$–$C_2$ | 538 | 16 | $C_1\cdots H_{3a}$ | 1204 | 25 |
| $C_2$–$C_3$ | 531 | 30 | $C_1\cdots H_{3b}$ | 1204 | 25 |
| C–S | 555 | 3 | $C_2\cdots H_4$ | 1008 | 19 |
| C–H | 780 | 86 | $C_2\cdots H_{6a}$ | 1077 | 43 |
| $C_1$–$C_3$ | 657 | 2 | $C_2\cdots H_{6b}$ | 1594 | −12 |
| $C_2\cdots C_6$ | 777 | 2 | $C_1\cdots H_4$ | 987 | 18 |
| $C_1\cdots C_4$ | 665 | −4 | $C_2\cdots H_{5a}$ | 1096 | 24 |
| $C_2\cdots C_5$ | 896 | −14 | $C_2\cdots H_{5b}$ | 1784 | −44 |
| $C_2\cdots S$ | 677 | −3 | $S\cdots H_1$ | 1089 | 14 |
| $C_1\cdots H_2$ | 1069 | 61 | $S\cdots H_{2a}$ | 1547 | −19 |
| $C_2\cdots H_1$ | 1046 | 32 | $S\cdots H_{2b}$ | 999 | 37 |
| $C_2\cdots H_3$ | 1068 | 78 | $H_{2a}\cdots H_{2b}$ | 1251 | 144 |

a) Calculated at 105 °C.

The $r_\alpha$ structures were determined by a least-squares analysis of the molecular intensities. A conventional diagonal weight matrix[16)] with unit elements in the range $6.3 \leq s \leq 26.7$ and smaller for smaller and larger scattering angles was used. The results are listed in Tables 4 and 5. The $r_g$ bond lengths derived from the $r_\alpha$ structure are also shown.

The error limits quoted in Tables 4 and 5 were estimated from random and systematic errors from various sources,[1,17)] including those originating from preceding assumptions. The structure of TBH given in Table 4 is regarded as the final result of the present study. The corresponding error matrix is listed in Table 6.

*Joint Analysis of Electron Diffraction Intensities and Rotational Constants for TN.* The rotational constants for the normal species of TN were reported by Hirota *et al.* from microwave spectroscopy.[3)] Their rotational constants for the ground vibrational state, $A_0$, $B_0$, and $C_0$, were transformed into $A_z$, $B_z$ and $C_z$ by making vibrational corrections.[18)] The electronic and centrifugal corrections were ignored. The uncertainties in the vibrational corrections were tentatively assumed to be 20%, and the uncertainties in the $A_0$, $B_0$, and $C_0$ constants were also taken into account in the total uncertainties in $A_z$, $B_z$ and $C_z$.

In order to check the consistency of the diffraction data with the spectroscopic data, the $r_\alpha$ structure determined from the diffraction data was extrapolated to zero kelvin[13,14)] by calculating the difference $r_\alpha^0$–$r_\alpha$. The anharmonic contribution to the difference was estimated on the basis of a diatomic approximation,[15)] while the harmonic contribution was derived from the force constants mentioned in the preceding subsection. The temperature effect on the bond angles was ignored.

As shown in Table 7, the rotational constants, $A_\alpha^0$, $B_\alpha^0$ and $C_\alpha^0$ calculated from the $r_\alpha^0$ structure agreed with their spectroscopic equivalents, $A_z$, $B_z$ and $C_z$ within their uncertainties. In general, if two bonds in a molecule with nearly equal distances are approximately parallel to different principal axes, the rotational constants with respect to these axes can be used for discriminating these bond lengths. For 7-thianorbornane, like 7-oxanorbornane,[1)] the rotational constants $A_z$ and $B_z$ are sensitive to the $C_2$–$C_3$ and $C_1$–$C_2$ bond lengths, respectively. Therefore, the rotational constants were taken into the least-squares analysis to complement the

TABLE 4. STRUCTURE AND MEAN AMPLITUDES OF 5-THIABICYCLO[2.1.1]HEXANE DERIVED FROM ELECTRON DIFFRACTION DATA[a)] (in Å and degrees)

| | $r_\alpha$ | $r_g$ | $\varepsilon^{b)}$ | | $r_\alpha^{c)}$ | $\varepsilon^{b,c)}$ | | $l$ | $\varepsilon^{b,c)}$ |
|---|---|---|---|---|---|---|---|---|---|
| ($C_1$–$C_2$, $C_2$–$C_3$)$_{av}$ | 1.535 | 1.539 | 0.016 | ∠$C_1$–$C_6$–$C_4$ | 85.4 | 1.6 | C–S | 0.057 | 0.006 |
| $C_1$–$C_6$ | 1.562 | 1.564 | 0.024 | ∠$C_1$–$C_2$–$C_3$ | 101.1 | 0.6 | C–H | 0.074 | 0.023 |
| C–S | 1.863 | 1.865 | 0.004 | ∠$C_2$–$C_1$–$C_6$ | 101.2 | 1.8 | $C_2\cdots S$ | 0.071 | 0.007 |
| C–H | 1.096 | 1.110 | 0.008 | ∠$C_2$–$C_1$–S | 103.6 | 1.2 | $C_6\cdots S$ | 0.050 | 0.011 |
| ∠C–S–C | 69.5 | | 0.6 | ∠$C_6$–$C_1$–S | 89.1 | 1.4 | | | |
| ∠($C_1SC_4$)-($C_1C_2C_3C_4$)[d)] | 115.2 | | 1.7 | ∠$C_2$–$C_1$–H | 119.2 | 0.5 | | | |
| | | | | ∠$C_1$–$C_2$–$H_2$ | 111.4 | 2.3 | | | |
| ∠($C_1C_6C_4$)-($C_1C_2C_3C_4$)[d)] | 116.1 | | 2.4 | ∠$C_1$–$C_6$–$H_6$ | 114.9 | 1.1 | | | |

a) Final result of the present study. b) Estimated limits of error. c) Calculated from the independent parameters. Uncertainties are estimated from those in the independent parameters. d) Dihedral angle.

TABLE 5. STRUCTURE AND MEAN AMPLITUDES OF 7-THIANORBORNANE DERIVED FROM ELECTRON DIFFRACTION[a)] (in Å and degrees)

| | $r_\alpha$ | $r_g$ | $\varepsilon^{b)}$ | | $l$ | $\varepsilon^{b)}$ |
|---|---|---|---|---|---|---|
| C–C | 1.541 | 1.545 | 0.004 | C–C | 0.058 | 0.009 |
| C–S | 1.834 | 1.836 | 0.007 | C–S | 0.064 | 0.008 |
| C–H | 1.098 | 1.112 | 0.008 | C–H | 0.087 | 0.013 |
| ∠C–S–C | 79.8 | | 0.8 | $C\cdots S$ | 0.077 | 0.006 |
| ∠($C_1C_2C_3C_4$)-($C_4C_5C_6C_1$)[c)] | 115.5 | | 1.5 | | | |
| ∠H–C–H | 108 | | 7 | | | |

a) Intermediate result. See Table 8 for the final result of the present study. b) Estimated limits of error. c) Dihedral angle.

TABLE 6. ERROR MATRIX FOR 5-THIABICYCLO[2.1.1]HEXANE[a)]

| | $k_1$ | $k_2$ | $x_1$ | $x_2$ | $x_2$ | $x_4$ | $x_5$ | $x_6$ | $x_7$ | $l_1$ | $l_2$ | $l_3$ | $l_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $k_1$ | 157 | 20 | −26 | 21 | 13 | 15 | −27 | 40 | −11 | −10 | 23 | −19 | 18 |
| $k_2$ | | 275 | −84 | 113 | −29 | −43 | 56 | 102 | 39 | 63 | 56 | 56 | 34 |
| $x_1$ | | | 31 | −39 | 9 | 14 | −18 | −37 | −20 | −19 | 17 | −17 | −4 |
| $x_2$ | | | | 53 | −12 | −19 | 27 | 49 | 26 | 26 | 23 | 23 | 14 |
| $x_3$ | | | | | 10 | 5 | −5 | −13 | 9 | −7 | −6 | −6 | 4 |
| $x_4$ | | | | | | 25 | −12 | −17 | −11 | −10 | −11 | −10 | −3 |
| $x_5$ | | | | | | | 25 | 24 | −32 | 13 | 11 | 13 | 10 |
| $x_6$ | | | | | | | | 50 | −17 | 23 | 21 | 20 | 6 |
| $x_7$ | | | | | | | | | 108 | 8 | 9 | 14 | 41 |
| $l_1$ | | | | | | | | | | 17 | 13 | 13 | 7 |
| $l_2$ | | | | | | | | | | | 26 | 11 | 8 |
| $l_3$ | | | | | | | | | | | | 19 | 4 |
| $l_4$ | | | | | | | | | | | | | 28 |

a) $k_1$, $k_2$=indices of resolution for the long and short camera length data (0.99±0.06, 0.92±0.08), respectively, $x_1$=the weighted average of $r(C_1-C_2)$ and $r(C_2-C_3)$, $x_2=r(C_1-C_6)$, $x_3=r(C-S)$, $x_4=r(C-H)$, $x_5=\angle C-S-C$, $x_6=\angle(C_1SC_4)-(C_1C_2C_3C_4)$, $x_7=\angle(C_1C_6C_4)-(C_1C_2C_3C_4)$, $l_1=l(C-S)$, $l_2=l(C-H)$, $l_3=l(C_2-S)$ and $l_4=l(C_6-S)$. Units ($\times 10^{-4}$) for the distances and mean amplitudes are Å, those for the angles are rad, and those for the indices are dimensionless.

TABLE 7. OBSERVED AND CALCULATED ROTATIONAL CONSTANTS FOR 7-THIANORBORNANE[a)] (in cm$^{-1}$)

| | $B_0$[b)] | $B_z$[c)] | $B_\alpha^0$[d)] | $B_{av}$[e)] |
|---|---|---|---|---|
| $A$ | 0.091741(6) | 0.091702(10) | 0.0919(5) | 0.091702(10) |
| $B$ | 0.088194(2) | 0.088169(5) | 0.0887(6) | 0.088169(5) |
| $C$ | 0.081402(2) | 0.081388(3) | 0.0810(4) | 0.081388(3) |

a) Uncertainties attached to the last significant digits are given in parentheses. b) Observed rotational constants for the ground vibrational state. Ref. 3. c) Zero-point average rotational constants calculated from $A_0$, $B_0$ and $C_0$ with corrections for vibrational effects. d) Rotational constants calculated from $r_\alpha^0$ parameters given in Table 5 determined in the analysis of electron diffraction intensities. Uncertainties are estimated from those in the $r_\alpha^0$ parameters. e) Best-fit rotational constants corresponding to the $r_{av}$ structure, listed in Table 8, derived from the combined analysis of diffraction and microwave data. Uncertainties represent 2.5 times the estimated standard deviations.

diffraction data.

For each least-squares calculation the standard deviations in the rotational constants were estimated from those in the $r_\alpha^0$ parameters by using the law of propagation of errors. The relative weights for the rotational constants were then adjusted in such a way that 2.5 times their standard deviations were approximately equal to their estimated uncertainties. The weights assigned in this way were $4\times10^8$, $1\times10^9$ and $3\times10^9$ for $A_z$, $B_z$ and $C_z$ respectively, in comparison with unit weights assigned to the molecular intensities from $s$=6.3 to 26.7 Å$^{-1}$. It was possible to release the constraint 6) on the C–C bond lengths by the joint use of the rotational constants and the electron diffraction

TABLE 9. OBSERVED MEAN AMPLITUDES FOR 7-THIANORBORNANE[a)] (in Å)

| | $l_{obsd}$[a)] | $l_{calcd}$[a),b)] |
|---|---|---|
| C–C[c)] | 0.054(9) | 0.054(5) |
| C–S | 0.061(8) | 0.056(6) |
| C–H | 0.081(13) | 0.078(8) |
| $C_2\cdots S$ | 0.075(5) | 0.068(14) |

a) Uncertainties attached to the last significant digits are given in parentheses. b) Taken from Table 2. Uncertainties are tentatively estimated to be about ±10% for C–C, C–S and C–H and about ±20% for $C_2\cdots S$. c) $l(C_1-C_2)$ and $l(C_2-C_3)$ are assumed to be equal to each other.

TABLE 8. STRUCTURE OF 7-THIANORBORNANE DERIVIVED FROM ELECTRON DIFFRACTION AND MICROWAVE DATA[a)] (in Å and degrees)

| | $r_{av}$ | $r_g$ | $\varepsilon$[b)] | | $r_{av}$[c)] | $\varepsilon$[b),c)] |
|---|---|---|---|---|---|---|
| $C_1-C_2$ | 1.535 | 1.538 | 0.006 | $\angle C_1-C_2-C_3$ | 105.2 | 0.5 |
| $C_2-C_3$ | 1.557 | 1.561 | 0.015 | $\angle C_2-C_1-C_6$ | 109.0 | 1.1 |
| C–S | 1.834 | 1.837 | 0.004 | $\angle C_2-C_1-S$ | 103.1 | 0.7 |
| C–H | 1.101 | 1.115 | 0.008 | $\angle H_1-C_1-S$ | 113.5 | 0.6 |
| $\angle$C–S–C | 80.2 | | 0.8 | $\angle C_1-C_2-H_2$ | 111.5 | 1.2 |
| $\angle(C_1C_2C_3C_4)-(C_4C_5C_6C_1)$[d)] | 115.0 | | 1.2 | | | |
| $\angle$H–C–H | 106 | | 5 | | | |

a) Final result of the present study. b) Estimated limits of error. c) Calculated from the independent parameters. Uncertainties are estimated from those in the independent parameters. d) Dihedral angle.

TABLE 10. ERROR MATRIX FOR 7-THIANORBORNANE[a)]

| | $k_1$ | $k_2$ | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $x_5$ | $x_6$ | $x_7$ | $l_1$ | $l_2$ | $l_3$ | $l_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $k_1$ | 150 | 78 | −44 | 64 | 24 | 21 | −60 | 58 | 116 | 5 | 13 | 18 | 25 |
| $k_2$ | | 321 | −16 | 46 | −39 | −29 | −29 | −29 | −42 | 59 | 61 | 76 | 44 |
| $x_1$ | | | 20 | −28 | −9 | −11 | 27 | −25 | −46 | 7 | −3 | −2 | −9 |
| $x_2$ | | | | 43 | 8 | 15 | −39 | 35 | 75 | −7 | 8 | 11 | 14 |
| $x_3$ | | | | | 12 | 3 | −12 | 15 | 27 | −7 | −8 | −9 | −3 |
| $x_4$ | | | | | | 24 | −14 | 16 | 50 | −7 | −4 | −9 | 4 |
| $x_5$ | | | | | | | 37 | −34 | −64 | 8 | −5 | −6 | −12 |
| $x_6$ | | | | | | | | 34 | 67 | −10 | −6 | −7 | 10 |
| $x_7$ | | | | | | | | | 177 | −21 | −8 | −13 | 23 |
| $l_1$ | | | | | | | | | | 13 | 11 | 14 | 8 |
| $l_2$ | | | | | | | | | | | 16 | 14 | 8 |
| $l_3$ | | | | | | | | | | | | 28 | 8 |
| $l_4$ | | | | | | | | | | | | | 12 |

a) $k_1$, $k_2$=indices of resolution for the long and short camera length data (1.03±0.08, 1.03±0.09), respectively, $x_1=r(C_1-C_2)$, $x_2=r(C_2-C_3)$, $x_3=r(C-S)$, $x_4=r(C-H)$, $x_5=\angle C-S-C$, $x_6=\angle(C_1C_2C_3C_4)-(C_4C_5C_6C_1)$, $x_7=\angle H-C-H$, $l_1=l(C-C)$, $l_2=l(C-S)$, $l_3=l(C-H)$ and $l_4=l(C\cdots S)$. Units ($\times 10^{-4}$) for the distances and mean amplitudes are Å, those for the angles are rad, and those for the indices are dimensionless.

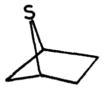
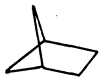
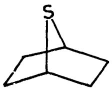
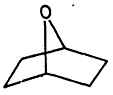
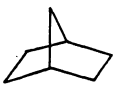
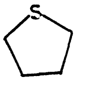
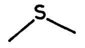
intensities. Including the indices of resolution for the long and short distance data, thirteen parameters were refined. The final structural parameters and mean amplitudes with estimated error limits are shown in Tables 8 and 9. The observed mean amplitudes for TBH and TN agree with the calculated mean amplitudes to within the limits of their uncertainties. The corresponding error matrix is given in Table 10.

## Discussion

The final structures of TBH and TN are compared with the structures of bicyclo[2.1.1]hexane,[19,20] norbornane,[21] 7-oxanorbornane,[1] tetrahydrothiophene[22] and dimethyl sulfide[23] in Table 11.

*C–S Bond Lengths and Sulfur Valence Angles.* The present study demonstrates unusual bond lengths and

TABLE 11. COMPARISON OF THE STRUCTURES OF RELATED MOLECULES[a)] (in Å and degrees)

| | $(C_1-C_2, C_2-C_3)_{av}$ | $C_1-C_2$ | $C_2-C_3$ | $C_1-C_6$ | C–S | $\angle C-S-C$ | $\angle C_1-C_6-C_4$[i)] | $\angle C_1-C_2-C_3$[i)] | $\theta$[j)] |
|---|---|---|---|---|---|---|---|---|---|
|  b) | 1.539(16) | | | 1.564(24) | 1.865(4) | 69.5(6) | 85.4(16) | 101.1(6) | 116.1(24) |
|  c) | 1.538(8)[k,l)] | | | 1.548(10)[k,l)] | | | 85.4(28)[l)] | 100.5(10)[l)] | 115.3(39)[l)] |
|  d) | 1.546(4) | 1.538(6) | 1.561(15) | | 1.837(4) | 80.2(8) | | 105.2(5) | 115.0(12) |
|  e) | 1.546(4) | 1.538(14) | 1.571(15) | | | | | 100.3(6) | 113.5(8) |
|  f) | 1.545(10) | 1.539(12) | 1.557(25) | 1.560(24)[m)] | | | | 103.3(7) | 113.1(18) |
|  g) | | | | | 1.841(2)[n)] | 93.4(5) | | | |
|  h) | | | | | 1.808(3) | 99.0(3) | | | |

a) Distances in $r_g$ and angles in $r_{av}$ ($r_\alpha$ for b and f, $r_a$ for c and g). Uncertainties represent estimated limits of error attached to the last significant digits. b) 7-Thiabicyclo[2.1.1]hexane, the present study. c) Bicyclo[2.1.1]hexane, Ref. 19. See also Ref. 20. d) 7-Thianorbornane, the present study. e) 7-Oxanorbornane, Ref. 1. f) Norbornane, Ref. 21. g) Tetrahydrothiophene, Ref. 22. h) Dimethyl sulfide, Ref. 23. i) Calculated from the independent parameters. j) Dihedral angles, $\angle(C_1C_6C_4)-(C_1C_2C_3C_4)$ for b and c, and $\angle(C_1C_2C_3C_4)-(C_4C_5C_6C_1)$ for d, e and f. k) Estimated from the $r_a$ distance reported in the literature by addition of $l^2/r_a$. l) Uncertainties have been re-estimated. m) The $C_1-C_7$ bond length in norbornane. n) Ref. 24.

angles in bicyclic compounds. The C–S bond length in TBH is longer than that in dimethyl sulfide[23] by 0.06 Å, and the C–S–C angle is smaller by about 30°. On the other hand, the C–S bond length and the C–S–C angle in TN are shorter by about 0.03 Å and larger by about 11°, respectively, than the corresponding values in TBH. This trend implies that intramolecular strain is much greater in TBH than in TN.

The present study also demonstrates a systematic decrease in the C–S–C angle in a series of sulfur substituted hydrocarbons: (a) acyclic, (b) five-membered ring and (c) bicyclic. The corresponding series of unsubstituted and oxygen substituted hydrocarbons showed a similar systematic trend in the C–C–C and C–O–C angles.[1] The C–S lengths do not show regular increases in the series of sulfur substituted hydrocarbons,[24] as do the C–C and C–O lengths in the series of unsubstituted and oxygen substituted hydrocarbons.[1] (See Table 11.)

*C–C Bond Lengths.* The essential features regarding the C–C bond lengths are the following:

1) The $C_1$–$C_6$ bond in TBH is longer than the weighted average of the $C_1$–$C_2$ and $C_2$–$C_3$ bond lengths. Similar trends were reported for norbornane.[21]

2) The average values of the $C_1$–$C_2$ and $C_2$–$C_3$ distances in TN, 7-oxanorbornane and norbornane are equal to one another to within their limits of error and about 0.01 Å longer than the normal single C–C bond length, whereas the corresponding average C–C bond length in TBH seems to be shorter and approximately equal to the normal C–C bond length.

3) For TN and 7-oxanorbornane the $C_1$–$C_2$ and $C_2$–$C_3$ bonds were separated by use of the rotational constants. The corresponding distances in these molecules are essentially equal to each other. The $C_1$–$C_2$ distances are similar to the normal single bond length, while the $C_2$–$C_3$ distances are about 0.02 Å longer and close to the $C_1$–$C_6$ distance in TBH or the $C_1$–$C_7$ distance in norbornane. The trend that the $C_2$–$C_3$ bond is longer than the $C_1$–$C_2$ bond has also been suggested for norbornane and bicyclo[2.2.2]octane.[25]

4) The C–C bond lengths in the six-membered rings in norbornane, 7-oxanorbornane and TN are remarkably similar in spite of the very different bond lengths and valence angles in the C–C–C, C–O–C and C–S–C bridges.

*Angles in the Rings.* The dihedral angles in norbornane and 7-oxanorbornane are nearly equal to each other and are about 2° smaller than that in TN. The $C_1$–$C_6$–$C_4$ angle in TBH seems to be essentially equal to that in bicyclo[2.1.1]hexane.[19] The $C_1$–$C_2$–$C_3$ angle in TN is about 5° larger than that in 7-oxanorbornane and about 3° larger than that in norbornane.

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## References

1) K. Oyanagi, T. Fukuyama, K. Kuchitsu, R. K. Bohn, and S. Li, This Bulletin, **48**, 751 (1975).

2) T. Fukuyama, K. Kuchitsu, Y. Tamaru, Z. Yoshida, and I. Tabushi, *J. Amer. Chem. Soc.*, **93**, 2799 (1971).

3) K. Irie, T. Tanaka, E. Hirota, Y. Tamaru, I. Tabushi, and Z. Yoshida, 27th Annual Meeting of the Chemical Society of Japan, Nagoya (1972), 1M02.

4) TBH: I. Tabushi, Y. Tamaru, and Z. Yoshida, *Tetrahedron Lett.*, **1970**, 2931. TN: E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966).

5) A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 72 (1971).

6) Y. Murata, K. Kuchitsu, and M. Kimura, *Japan. J. Appl. Phys.*, **9**, 591 (1970).

7) M. Tanimoto, K. Kuchitsu, and Y. Morino, This Bulletin, **43**, 2776 (1970).

8) Y. Morino, K. Kuchitsu, and T. Fukuyama, *ibid.*, **40**, 423 (1967).

9) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).

10) Numerical experimental data of the leveled total intensity and the background have been deposited with the Chemical Society of Japan (Document No. 7609).

11) H. Takahashi and T. Shimanouchi, *J. Mol. Spectrosc.*, **13**, 43 (1964).

12) M. Ohsaku, Y. Shiro, and H. Murata, This Bulletin, **46**, 1399 (1973).

13) K. Kuchitsu and S. Konaka, *J. Chem. Phys.*, **45**, 4342 (1966).

14) K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Elsevier, Amsterdam (1972), Chapter 12.

15) K. Kuchitsu, This Bulletin, **40**, 505 (1967).

16) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

17) K. Kuchitsu, "Molecular Structures and Vibrations," ed. by S. J. Cyvin, Elsevier, Amsterdam (1972), Chapter 10.

18) M. Toyama, T. Oka, and Y. Morino, *J. Mol. Spectrosc.*, **13**, 193 (1964).

19) G. Dallinga and L. H. Toneman, *Rec. Trav. Chim.*, **86**, 171 (1967).

20) J. F. Chiang, *J. Amer. Chem. Soc.*, **93**, 5044 (1971). The structure of bicyclo[2.1.1]hexane reported in this reference is in significant discrepancy with that in Ref. 19. The analysis of Ref. 20 in which highly correlated structural parameters are claimed to be determined uniquely seems to be questionable.

21) A. Yokozeki and K. Kuchitsu, This Bulletin, **44**, 2356 (1971).

22) Z. Náhlovska, B. Náhlovsky, and H. M. Seip, *Acta Chem. Scand.*, **23**, 3534 (1969).

23) T. Iijima, private communication.

24) The C–S bond length reported in Ref. 22 seems to be slightly too long. K. Takemura, T. Fukuyama, and K. Kuchitsu, unpublished data (1975).

25) A. Yokozeki, K. Kuchitsu, and Y. Morino, This Bulletin, **43**, 2017 (1970).