# *Infrared Spectra and Normal Vibrations of Thioamides. III. N-Methylthioformamide and N-Methylthioacetamide*

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(Received February 2, 1962)

It has been shown in preceding papers[1,2),*1] that a normal coordinate analysis of the $HCSNH_2$ and $CH_2CSNH_2$ molecules can be made quite successfully by applying the Urey-Bradley force field[3)]. The nature of normal vibrations have been clarified, and the values of the force constants have now been settled for these primary thioamides. The work has also been extended to secondary thioamides, RCSNHR′, and in this paper the results obtained for *N*-methylthioformamide and *N*-methylthioacetamide will be presented.

*N*-Methylthioformamide and *N*-methylthioacetamide, as well as their *N*-deuterated analogues, were prepared, and their infrared spectra were measured in the solid and liquid states and in solution. It is now well accepted that the simple secondary amides, RCONHR′, predominantly take the planar configurations in which R and R′ are in the trans-position with regard to each other[4)]. It will be shown in the present investigation that the vibrational spectra of secondary thioamides are also interpreted satisfactorily in terms of the trans planar models. The in-plane normal vibrations of $HCSNHCH_3$ and $HCSNDCH_3$ have been calculated from the force constants directly transferred from $HCSNH_2$ (I) and $HCONHCH_3$[5)]; the calculated frequencies for the trans configuration agree well with the observed frequencies.

In the present paper, the results of these measurements and calculations are reported. Based on these results, the nature of the normal vibrations and the problem of a stable configuration for the secondary thioamides are discussed.

## Experimental

**Materials.**—*N-Methylthioacetamide* $CH_3CSNHCH_3$. —This compound was prepared by heating *N*-methylacetamide, with phosphorus pentasulfide suspended in benzene at about 50°C for 3 hr.[6)] The sample was purified by recrystallization from ether containing petroleum ether; m. p., 59°C (uncorr.).

*N-Methylthioformamide* $HCSNHCH_3$. — This was prepared from *N*-methylformamide by a method analogous to that used for *N*-methylthioacetamide. This compound is not as stable as *N*-methylthioacetamide, and it was usually kept in a refrigerator as an ethereal solution. When it was distilled, it showed obvious signs of decomposition, even at a reduced pressure. Therefore, it was purified by recrystallization from ether containing petroleum ether at about −50°C.

The exchange reaction with deuterium oxide was used to replaced the amide hydrogen atom with deuterium.

**Infrared Spectra.** — The infrared measurements of $HCSNHCH_3$ were made in the liquid and solid states and in solutions; the results are given in Figs. 1 and 3, and the observed frequencies, in Table I(a). Those of $HCSNDCH_3$ are given in Figs. 2 and 3. A low temperature cell[7)] cooled with a mixture of dry ice and methanol was used to obtain the spectra in the solid state. The infrared measurements of $CH_3CSNHCH_3$ were also made in the solid and liquid states and in solutions; the results are given in Figs. 4 and 5, and the observed frequencies, in Table I(b). Those of the deuterated species are given in Figs. 4 and 5. The spectra in

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1) I. Suzuki, This Bulletin, 35, 1286 (1962).

2) I. Suzuki, ibid., 35, 1449 (1962).

[*1] Hereafter referred to as (I) and (II).

3) T. Shimanouchi, *J. Chem. Phys.*, 17, 245, 734, 848 (1945).

4) For example, T. Miyazawa, T. Shimanouchi and S. Mizushima, ibid., 24, 408 (1956); 29, 611 (1958).

5) I. Suzuki, This Bulletin, 35, 540 (1962).

6) I. L. Knunyants and L. V. Razadovskaya, *J. Gen. Chem.* (*U. S. S. R.*), 9, 557 (1939) (*Chem. Abstr.*, 34, 391 (1940)).

7) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 76, 821 (1955).

TABLE I(a). THE OBSERVED FREQUENCIES (IN $\mathrm{cm^{-1}}$) OF $\mathrm{HCSNHCH_3}$

| Solid (−50°) | Liquid | Solution<br>$\mathrm{CCl_4}$ concn. | Solution<br>or | Solution<br>$\mathrm{CS_2}$ dil. | Solution<br>$\mathrm{CHCl_3}$ | Assignment |
|---|---|---|---|---|---|---|
| 3160 | 3230 | 3233<br>−70 | | 3434 | 3415 | $\nu(\mathrm{NH})$ |
| 3047 | 3047 | | | | | |
| 2960 | 2985 | | 2963 | | 2965 | $\nu_{\mathrm{a}}(\mathrm{CH_3})$ |
| | | | 2933 | | | $\nu_{\mathrm{s}}(\mathrm{CH_3})$ |
| 2850 | | | | | | |
| 1550 | 1537 | | | | 1525 | $\nu(\mathrm{CN})+\delta(\mathrm{NH})$ |
| 1492 | 1479 | | 1482 | | 1480 | $\delta_{\mathrm{a}}(\mathrm{CH_3})+\delta(\mathrm{CH})+\delta(\mathrm{NH})$ |
| 1470 | 1463 | | 1460 | | 1461 | $\delta_{\mathrm{a}}(\mathrm{CH_3})$ (A′′) |
| 1440 | 1443 | | | | (1437) | $\delta(\mathrm{CH})+\nu(\mathrm{CN})$ |
| 1392 | 1393 | | 1399 | | 1394 | $\delta_{\mathrm{s}}(\mathrm{CH_3})$ |
| 1370 | | | 1348 | | | |
| 1308 | 1297 | 1300 | | 1277 | 1288 | $\delta(\mathrm{CH})+\delta(\mathrm{NH})+\nu(\mathrm{CN})$ |
| 1138 | 1136 | | 1135 | | 1137 | $r(\mathrm{CH_3})+\nu(\mathrm{C'N})$ |
| | (1010) | | 1025 | | 1020 | $\pi(\mathrm{CH})$ (A′′) |
| 992 | 987 | | 992 | | 992 | $r(\mathrm{CH_3})+\nu(\mathrm{C'N})+\nu(\mathrm{CS})$ |
| 985<br>946 | | | | | | |
| 912 | 920 | 927 | | 915 | 923 | |
| 874<br>865 | 868 | 873 | | 878 | 873 | $\nu(\mathrm{CS})+\nu(\mathrm{C'N})$ |
| 739 | 680 | | 667 ($\mathrm{CH_3CN}$) | | | $\pi(\mathrm{NH})$ (A′′) |
| | 600 | | 606 ($\mathrm{CH_3CN}$) | | | $\delta(\mathrm{NCS})-\delta(\mathrm{CNC'})$ |
| | 467 | | 467 ($\mathrm{CH_3CN}$) | | | |
| | 363 | | 357 ($\mathrm{CH_3CN}$) | | | $\tau(\mathrm{CN})$ (A′′) |
| | $(200)_{\mathrm{calcd}}$ | | | | | $\delta(\mathrm{NCS})+\delta(\mathrm{CNC'})$ |

TABLE I(b). THE OBSERVED FREQUENCIES (IN $\mathrm{cm^{-1}}$) OF $\mathrm{CH_3CSNHCH_3}$

| Solid | Liquid | Solution<br>$\mathrm{CCl_4}$, $\mathrm{CS_2}$ | Solution<br>$\mathrm{CHCl_3}$ | Solution<br>$\mathrm{CH_3CN}$ | Assignment |
|---|---|---|---|---|---|
| 3207 | 3283 | 3428<br>3240 | 3425<br>3250 | | $\nu(\mathrm{NH})$ |
| 3077 | 3063 | (3045) | (3050) | | |
| 3019 | | | | | |
| 2977 | 2985 | | | | $\delta_{\mathrm{a}}(\mathrm{CH_3})_{\mathrm{N\ and\ C}}$ |
| 2935 | 2928 | 2930 | | | $\delta_{\mathrm{s}}(\mathrm{CH_3})_{\mathrm{N\ and\ C}}$ |
| 1565 | 1547 | | 1534 | | $\delta(\mathrm{NH})+\nu(\mathrm{CN})$ |
| 1473 | 1460 | | (1469) | | $\delta_{\mathrm{a}}(\mathrm{CH_3})_{\mathrm{C}}$ |
| 1425 | 1438 | | 1438 | | $\delta_{\mathrm{a}}(\mathrm{CH_3})_{\mathrm{N}}$ |
| 1370 | | | 1375 sh | | $\delta_{\mathrm{s}}(\mathrm{CH_3})_{\mathrm{N}}$ |
| | 1360 | | | | |
| 1357 | | 1348 | 1360 | | $\delta_{\mathrm{s}}(\mathrm{CH_3})_{\mathrm{C}}$ and $\nu(\mathrm{CN})+\delta(\mathrm{NH})$ |
| 1243 | 1242 | (1246) | | | |
| 1211 | 1210 | 1212 | | | |
| 1099 | 1100 | 1100 | 1099 | | $\nu(\mathrm{CC})+\nu(\mathrm{CS})+r(\mathrm{CH_3})_{\mathrm{N}}$ |
| 1074 | (1060) | (1055 ?) | | | |
| 1023 | 1020 | 1038 | 1022 | | $r(\mathrm{CH_3})_{\mathrm{N}}$ and $r(\mathrm{CH_3})_{\mathrm{C}}$ |
| 955 | 950 | 945 | 952 | | $\nu(\mathrm{C'N})+\nu(\mathrm{CS})$ |
| 746 | 690 | | | 690 br. | $\pi(\mathrm{NH})$ |
| 684 | 690 | 699 | | 703 | $\nu(\mathrm{CS})+\nu(\mathrm{CC})$ |
| 559 | 555 | | | 552 | $\delta(\mathrm{NCS})-\delta(\mathrm{CNC'})$ |
| 538 | 533 | | | 532 | $\pi(\mathrm{CC'})$ |
| 503 | (503) | | | | |
| 374 | 370 | | | | $\delta(\mathrm{CC'})$ |
| 387 | (287) | | | | $\delta(\mathrm{NCS})+\delta(\mathrm{CNC'})$ |

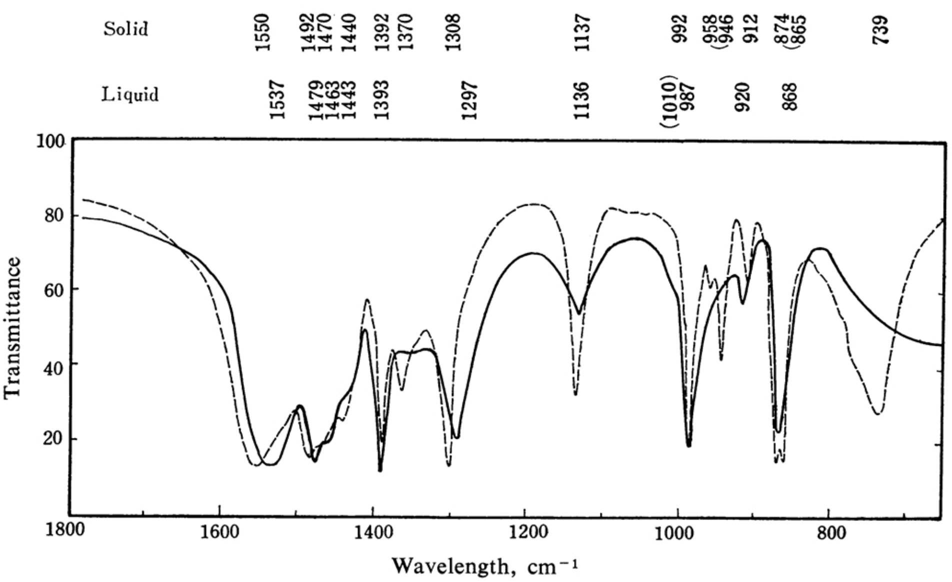

Fig. 1. Infrared spectra of $HCSNHCH_3$ in the liquid state (solid line) and in the solid state (broken line) in the region from 1800 to 650 cm$^{-1}$.

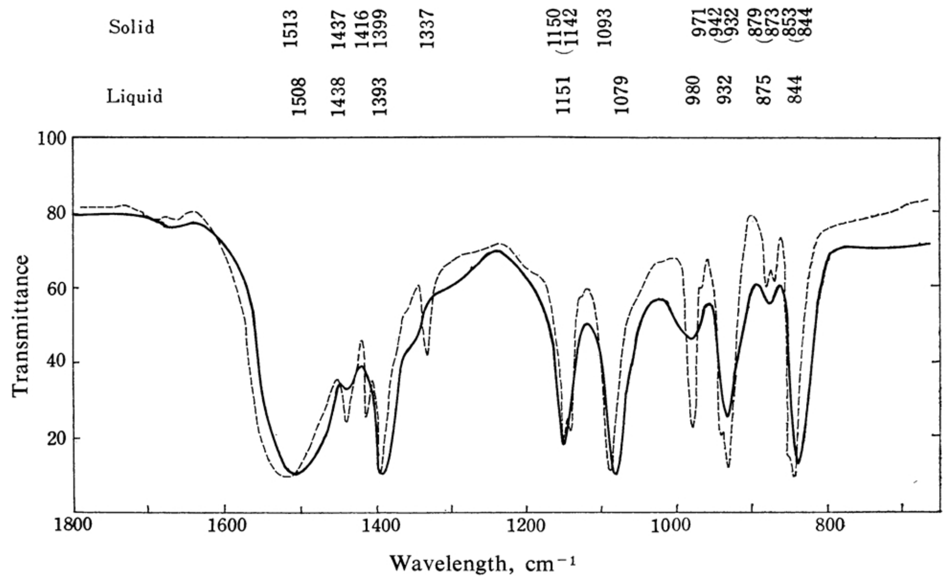

Fig. 2. Infrared spectra of $HCSNDCH_3$ in the liquid state (solid line) and in the solid state (broken line) in the region from 1800 to 650 cm$^{-1}$.

the solid state were obtained as Nujol or hexachlorobutadiene mulls. A small heating cell was used to measure the spectrum in the liquid state. Carbon tetrachloride, carbon disulfide or chloroform were used as solvents in the region from 3500 to 800 cm$^{-1}$ and acetonitrile in the region from 800 to 400 cm$^{-1}$.

The spectrophotometers used in the present work are the same as those described in (I). In addition, a high-resolution Perkin-Elmer 112G grating spectrophotometer equipped with a KBr fore-prism was employed for the measurement of the NH stretching bands in carbon tetrachloride in the $3\mu$ region. The results are given in Fig. 6.

## Normal Coordinate Treatment

The normal coordinate treatments were undertaken for the in-plane vibrations of $HCSNHCH_3$ and $HCSNDCH_3$ as a nine-body problem, assuming a trans planar structure for the molecule which was analogous to $HCONHCH_3$[5]. The calculation procedures

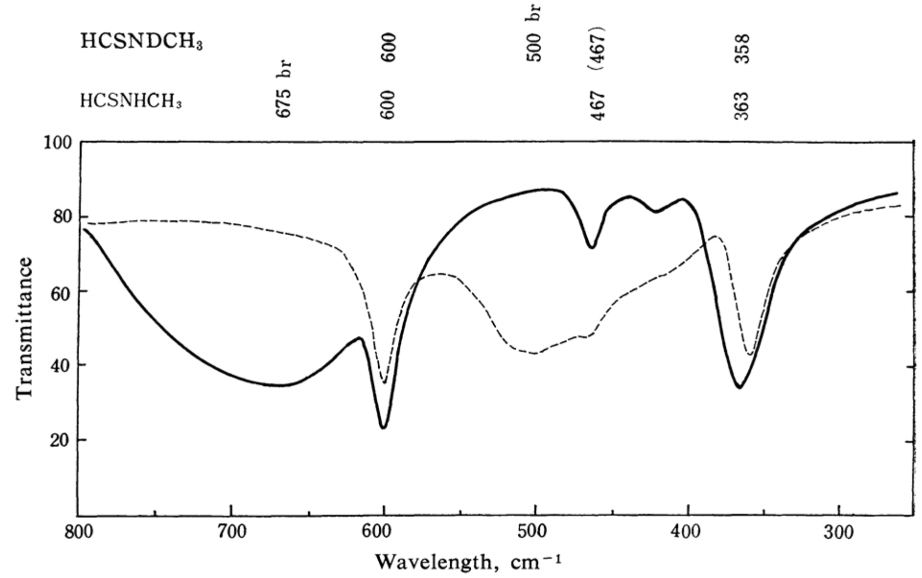

Fig. 3. Infrared spectra of $HCSNHCH_3$ (solid line) and $HCSNDCH_3$ (broken line) in the liquid state in the region from 800 to 260 $cm^{-1}$.

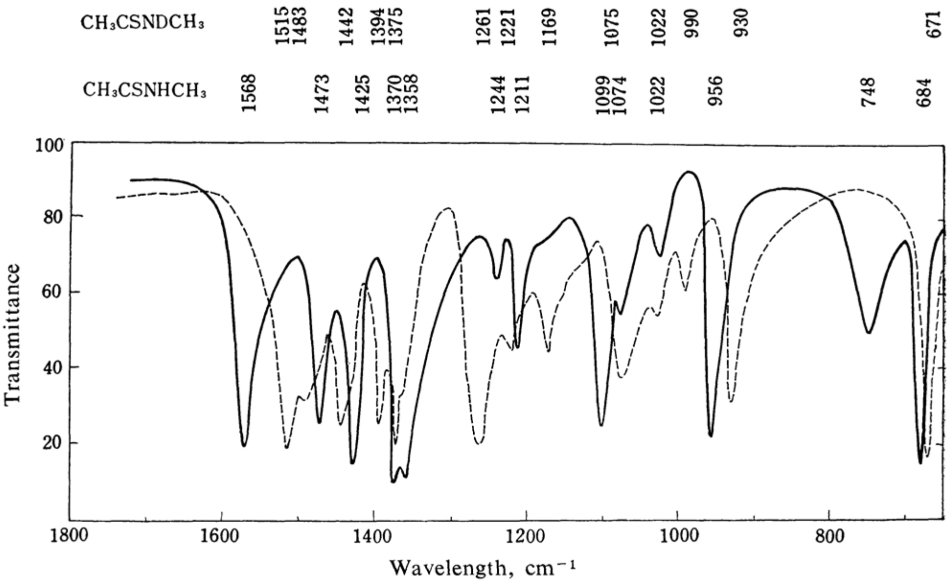

Fig. 4. Infrared spectra of $CH_3CSNHCH_3$ (solid line) and $CH_3CSNDCH_3$ (broken line) in the solid state in the region from 1800 to 650 $cm^{-1}$.

are similar to those for the $HCONHCH_3$ molecule and do not be described here. The structural parameters used in the calculation are the bond lengths of $r(C=S)=1.713\,Å$, $r(C-N)=1.324\,Å$, $r(C'-N)$[*2] $=1.47\,Å$, $r(C'-H)=r(C-H)=1.07\,Å$, and the bond angles of 120° for those around the C and N atoms and of 109°47′ for those around the C′ atom. The symmetry coordinates used in the calculation are listed in Table II; the combinations of

TABLE II. SYMMETRY COORDINATES

| $S_i$ | Vibrational mode | Abbr. |
|---|---|---|
| $S_1$ | CS stretching | $\nu(CS)$ |
| $S_2$ | CN stretching | $\nu(CN)$ |
| $S_3$ | C′N stretching | $\nu(C'N)$ |
| $S_4$ | NH deformation | $\delta(NH)$ |
| $S_5$ | CH deformation | $\delta(CH)$ |
| $S_6$ | CNC′ deformation | $\delta(CNC')$ |
| $S_7$ | NCS deformation | $\delta(NCS)$ |
| $S_8$ | $CH_3$ sym. deformation | $\delta_s(CH_3)$ |
| $S_9$ | $CH_3$ rocking | $r(CH_3)$ |
| $S_{10}$ | $CH_3$ asym. deformation | $\delta_a(CH_3)$ |

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[*2] C and C′ denote the thiocarbonyl and methyl carbon atoms respectively.

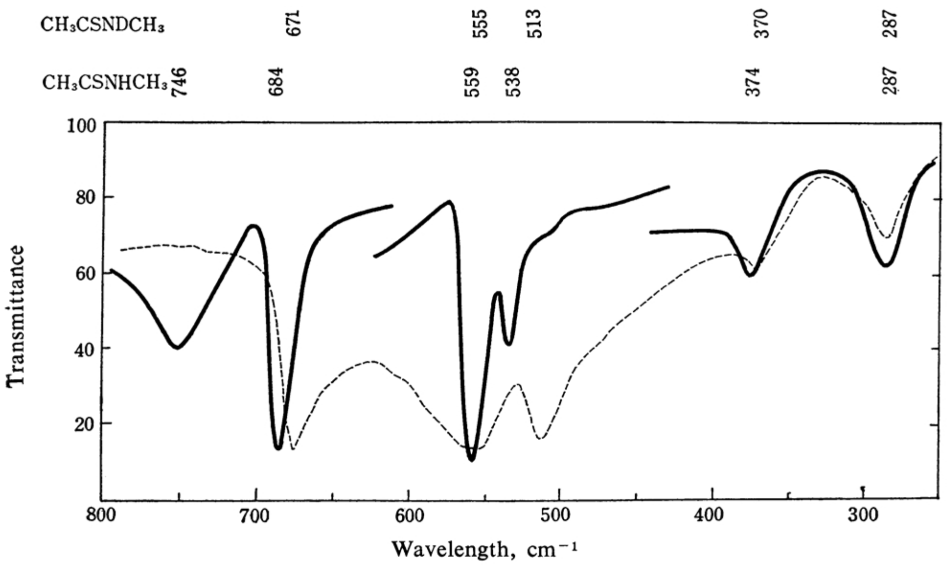

Fig. 5. Infrared spectra of CH$_3$CSNHCH$_3$ (solid line) and CH$_3$CSNDCH$_3$ (broken line) in the solid state in the region from 800 to 260 cm$^{-1}$.

TABLE III. FORCE CONSTANTS (md./A)

| | | | | | | |
|---|---|---|---|---|---|---|
| | $K_{CN}$ | 6.15 | $H_{CNC'}$ | 0.35 | $F_{C\cdots C'}$ | 0.30 |
| I | $K_{C'N}$ | 3.15 | $H_{CNH}$ | 0.30 | $F_{C\cdots H}$ | 0.46 |
| | | | $H_{C'NH}$ | 0.25 | $F_{C'\cdots H}$ | 0.36 |
| | $K_{CS}$ | 3.95 | $H_{NCS}$ | 0.15 | $F_{N\cdots S}$ | 1.02 |
| II | | | $H_{NCH}$ | 0.17 | $F_{N\cdots H}$ | 0.74 |
| | | | $H_{HCS}$ | 0.13 | $F_{H\cdots S}$ | 0.60 |
| III | $\kappa$ | −0.05 | $H_{NC'H}$ | 0.28 | $F_{N\cdots H}$ | 0.52 |
| | | (md.·A) | $H_{HC'H}$ | 0.43 | $F_{H\cdots H}$ | 0.05 |

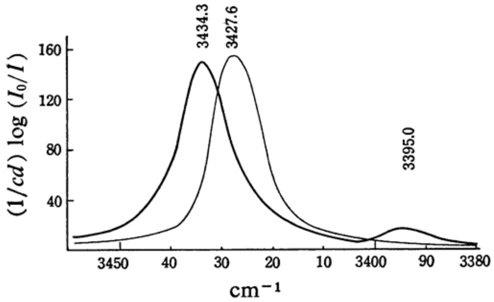

Fig. 6. Infrared absorptions of HCONHCH$_3$ (——) and CH$_3$CSNHCH$_3$ (━━) in carbon tetrachloride solutions in the region from 3460 to 3380 cm$^{-1}$ (The effective slit width is about 1.8 cm$^{-1}$).

the interal coordinates in each symmetry coordinate are given in Ref. 5 and so are not reproduced here. Four higher frequencies corresponding to the CH and NH(D) steretching vibrations are separated from the lower frequencies[8].

**Force Constants.** — As in (I) and (II), the Urey-Bradley force field was employed in the calculation. In Table III, the values of the force constants used are listed. They were determined by the following methods: the values of the force constants in group I were directly transferred from the HCONHCH$_3$[5] molecule, while those in group II are from the HCSNH$_2$ molecule (I). The force constants belonging to group III are related to the N–CH$_3$ part of the molecule. They are also transferred from HCSNHCH$_3$, but slightly modified values were used[*3].

**Results of Calculation.**—The computed frequencies from the force constants given in Table III are shown in Tables IV (a) and (b). They show a surprisingly good agreement with the observed frequencies, with a maximum deviation of 3.6%. The agreement is so good that the refinement of the force constants is unnecessary

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[8] E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 96 (1941).

[*3] The Urey-Bradley force constants have been obtained in our laboratory for a number of compounds containing methyl groups. The set of $H_{HCH}$=0.43 md./A, $F_{H\cdots H}$=0.03 md./A and $\kappa$=−0.05 md.·A has been found to be the best choice for explaining the frequency data.

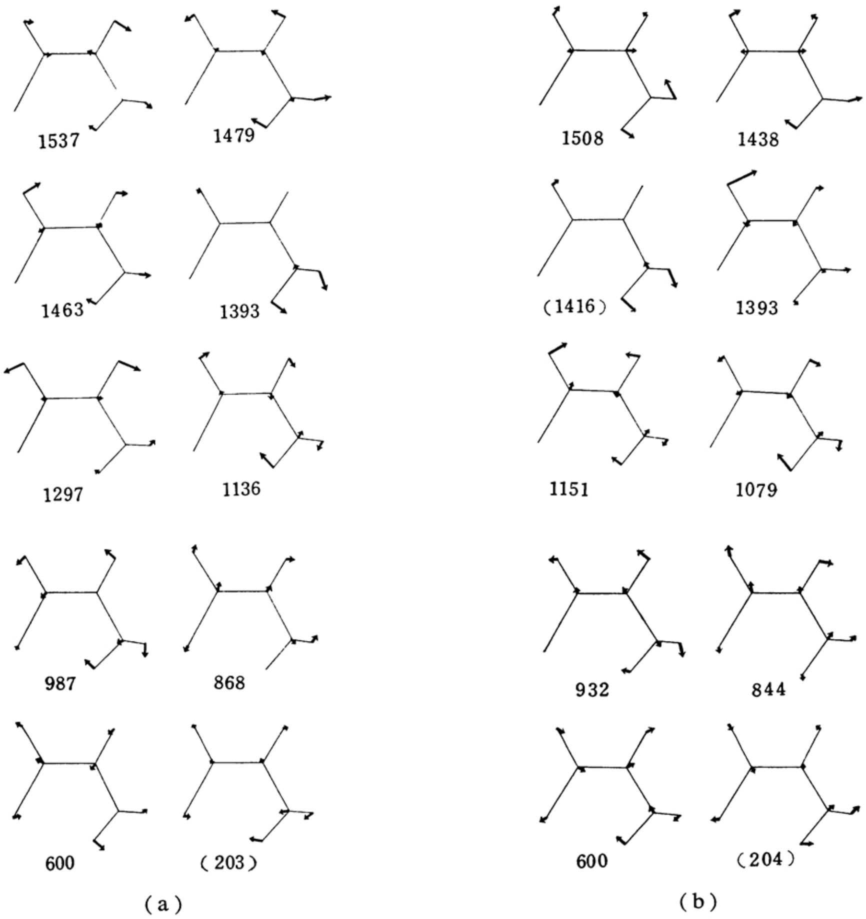
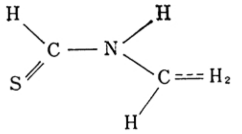
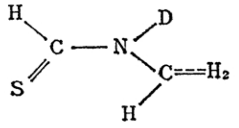


Fig. 7. The in-plane normal modes of *N*-methylthioformamides in Cartesian diplacement vectors projected to the molecular plane (A/unit change in normal coordinate).

(a) $HCSNHCH_2$:



(b) $HCSNDCH_3$:



for the present purposes. Tables IV (a) and (b) list the potential energy distributions among the symmetry coordinates, as well as the signs of the corresponding elements of the *L* matrix. The Cartesian displacement vectors[*4] obtained from the $L^x$ matrix have also been calculated; they are given in Figs. 7 (a) and (b).

The numerical computations were carried out with a PC-1 computer; the routines and methods of calculations are described in Refs. 9 and 10 and so are not described here.

## Discussion

**Possible Rotational Isomers.** — As shown in (I) and (II), the C–N bonds of the thioamide molecules possess a considerable double-bond character, and the molecules take approximately planar configurations. Therefore, the secondary thioamides have two possible configurations, cis and trans, in which the amide hydrogen and thiocarbonyl sulfur atoms take, respectively, the cis and trans positions with regard to each other. Russell and Thompson[11)] have proposed that the two closely situated NH stretching bands of the secondary amides in dilute carbon tetrachloride solutions arise from these two isomers;

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[*4] Special treatment is necessary to calculate the $L^X$ matrix when higher frequencies are separated from lower ones. The details were given in (II).

9) T. Shimanouchi and I. Suzuki, *J. Mol. Spectroscopy*, **6**, 277 (1961).

10) T. Shimanouchi and I. Suzuki, ibid., **8**, 222 (1962).

11) R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956).

TABLE IV. THE OBSERVED AND CALCULATED FREQUENCIES, PERCENT DEVIATIONS, AND POTENTIAL ENERGY DISTRIBUTIONS AMONG THE SYMMETRY COORDINATES, $(F_{ii}L_{is}^2/\lambda_s \times 100)$

(a) $HCSNHCH_3$

| $Q_i$ | $\nu_{obs}$ | $\nu_{calcd}$ | $\Delta\nu$ | $\Delta$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ | $S_9$ | $S_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Q_1$ | 1537 | 1539 | − 2 | 0.1 | 1* | **44** | 7* | **50** | 0* | 0* | 1* | 1* | 6 | 3 |
| $Q_2$ | 1479 | 1476 | + 3 | 0.2 | 2* | 1 | 1 | 15* | 10* | 0* | 0 | 0 | 11 | **59** |
| $Q_3$ | 1443 | 1442 | + 1 | 0.1 | 10 | **25*** | 0* | 5 | **55** | 2 | 0* | 0* | 1 | **19** |
| $Q_4$ | 1393 | 1405 | − 8 | 0.5 | 0 | 0 | 9* | 0 | 0 | 0 | 0* | **100** | 0 | 0* |
| $Q_5$ | 1297 | 1285 | +12 | 0.8 | 2* | **21** | 3* | **26*** | **35** | 0* | 0* | 0* | 0 | 1* |
| $Q_6$ | 1136 | 1097 | +39 | 3.6 | 1* | 0* | **27** | 0 | 2 | 11* | 5 | 0 | **45** | 10* |
| $Q_7$ | 987 | 987 | 0 | 0 | **22** | 3* | **29*** | 3* | 1* | 2 | 4* | 0* | **32** | 7* |
| $Q_8$ | 868 | 883 | −15 | 1.8 | **57** | 10 | **24** | 1* | 0 | 1 | 9* | 0 | 1* | 0 |
| $Q_9$ | 600 | 589 | +11 | 1.8 | 12* | 0 | 6 | 0* | 0* | **35** | **35*** | 0 | 4 | 1* |
| $Q_{10}$ | — | 204 | — | — | 0* | 1 | 0 | 0* | 0* | **52** | **49** | 0 | 1 | 0* |

(b) $HCSNDCH_3$

| $Q_i$ | $\nu_{obs}$ | $\nu_{calcd}$ | $\Delta\nu$ | $\Delta$ | $S_1$ | $S_2$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_7$ | $S_8$ | $S_9$ | $S_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Q_1$ | 1508 | 1503 | + 5 | 0.3 | 4* | **50** | 4* | 4 | 8* | 1* | 0* | 0* | 13 | **27** |
| $Q_2$ | 1438 | 1452 | −14 | 1.0 | 4 | **31*** | 2 | 3* | 11 | 1 | 0 | 1 | 4 | **54** |
| $Q_3$ | (1416) | 1406 | — | — | 0* | 0 | 5* | 0* | 3* | 0* | 0 | **101** | 0* | 0* |
| $Q_4$ | 1393 | 1395 | − 2 | 0.2 | 3 | 3 | 13* | 11 | **70** | 1 | 2* | 3 | 0 | 1* |
| $Q_5$ | 1151 | 1114 | +37 | 3.3 | 18 | 4* | 20 | 24 | 11* | 9 | 6* | 0 | 8* | 2 |
| $Q_6$ | 1079 | 1068 | +11 | 1.0 | 8 | 5* | 3 | 15 | 0* | 2* | 0 | 0 | **57** | 12* |
| $Q_7$ | 932 | 922 | +10 | 1.1 | 0 | 4 | **50** | **23** | 0 | 1* | 0 | 0 | 14 | 3* |
| $Q_8$ | 844 | 863 | −19 | 2.3 | **57** | 8 | 5 | **21*** | 0 | 3 | 11* | 0* | 0 | 0* |
| $Q_9$ | 600 | 584 | +16 | 2.7 | 13* | 0 | 5 | 0* | 0* | **35** | **34*** | 0 | 4 | 1* |
| $Q_{10}$ | — | 204 | — | — | 0* | 1 | 0 | 0* | 0* | **50** | **52** | 0 | 1 | 0* |

$\Delta\nu = \nu_{obs} - \nu_{calcd}, \quad \Delta = |\Delta\nu|/\nu_{obs}$

* The asterisk means that the corresponding $\boldsymbol{L}$ matrix element is negative.

the band with a higher frequency corresponds to the NH stretching vibration of the trans form, and the band with a lower frequency, to that of the cis form. This proposal was supported by our dielectric and infrared measurements of some anilides over a wide range of concentrations[12,13], although there is a certain limitation in applying the rule, especially to aromatic amides[14]. It was also shown that the rule is applicable not only to secondary amides but also to thioamides[13].

The infrared absorption curves of $HCSNHCH_3$ and $CH_3CSNHCH_3$ in dilute carbon tetrachloride solutions are shown in Fig. 6. Only a single absorption peak is observed at 3427.6 $cm^{-1}$ for $CH_3CSNHCH_3$. In addition to the main peak at 3434.3 $cm^{-1}$, $HCSNHCH_3$ shows a satellite peak at a lower frequency. The positions and the relative intensities[*5] of these two bands correspond well to those of $HCONHCH_3$. Therefore, it can be concluded that $CH_3CSNHCH_3$ takes the trans configuration, even in a dilute non-polar solvent, and that $HCSNHCH_3$ takes both trans and cis forms, of which the former is predominant. In analogy with the secondary amides, these facts indicate that thioamides are also in the trans form in the condensed phases. The calculations of the normal vibrations of $HCSNHCH_3$ and $HCSNDCH_3$ described below also indicate that the vibrational spectra of these molecules are satisfactorily explained by assuming that the molecules are predominantly in the trans form.

**Assignments of the Observed Frequencies.**—As has already been stated, the computed frequencies of $HCSNHCH_3$ and $HCSNDCH_3$ given in Tables IV (a) and (b) are in good agreement with the results of observation. Not only does it indicate the excellent transferability of the Urey-Bradley force constants, but it also shows that the assumption of the trans planar model for the molecule is generally correct. Therefore, the potential energy distributions among the symmetry coordinates given in Tables IV (a) and (b), as well as the Cartesian

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[12] I. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 353, 697 (1959).

[13] I. Suzuki, M. Tsuboi, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **16**, 471 (1960).

[14] I. Suzuki, M. Tsuboi and T. Shimanouchi, ibid., **16**, 467 (1960).

[*5] The relative intensity of the satellite band to the main band is a little stronger than that of $HCONHCH_3$; this is consistent with the results obtained from anilides and thioanilides[12,13].

displacement vectors given schematically in Figs. 7 (a) and (b), can be considered to represent the quantitative assignments of the observed frequencies.

Next, the out-of-plane vibrations should be treated in order to complete the vibrational assignments of *N*-methylthioformamide. Of seven out-of-plane vibrations, four are chiefly associated with the $CH_3$ group vibrations. The methyl asymmetric stretching, asymmetric deformation and rocking vibrations are expected to occur around the corresponding in-plane vibrations. The methyl torsional vibration is expected to appear at a much lower frequency and to lie beyond the limits of the present investigation. The remaining three are the NH and CH out-of-plane and CN torsional vibrations, $\pi$(NH), $\pi$(CH) and $\tau$(CN). The 680 and 363 $cm^{-1}$ bands of $HCSNHCH_3$ correspond well with those at 720 and 353 $cm^{-1}$ of $HCONHCH_3$ in their positions, intensities, and spectral changes due to *N*-deuteration and to the alternation of the states of aggregation as well. They are assigned, respectively, to the $\pi$(NH) and $\tau$(CN) vibrations[*6]. The assignment of the $\pi$(CH) vibration is slightly ambiguous. In $HCSNH_2$ it was found at 985 $cm^{-1}$, and a band found at 980 $cm^{-1}$ of $HCSNDCH_3$ is probably to be assigned to this vibration. In $HCSNHCH_3$, there is a strong band at 987 $cm^{-1}$ belonging to one of the in-plane vibrations. Therefore, it is not clear whether a weak shoulder band at 1010 $cm^{-1}$ is to be ascribed to the $\pi$(CH) mode or it overlaps the strong band mentioned above. In the last column of Table I (a), the approximate assignments of the observed frequencies are given.

If we combine the results of the normal coordinate analysis of $HCSNHCH_3$ with those of $CH_3CSNH_2$ and $CH_3CONHCH_3$[4)], it is not difficult to assign the observed bands of $CH_3CSNHCH_3$. The results of these vibrational assignments are given in the last column of Table I (b). In the next section vibrational assignments of some bands in $CH_3CSNHCH_3$ and $CH_3CSNDCH_3$ are discussed in connection with the characteristic frequencies of secondary thioamides.

**The Characteristic Frequencies of Secondary Thioamides.** — The nature of some vibration bands characteristic of the secondary thioamides will now be discussed in detail on the basis of the assignments described in the previous section.

**The Band around 1550 $cm^{-1}$.**—As can be seen from Table IV (a) and Fig. 7 (a), the band at 1537 $cm^{-1}$ of $HCSNHCH_3$ is assigned to the mixed vibration of the $\nu$(CN) and $\delta$(NH). The nature and the frequency of the band, as well as its change due to the states of aggregation, correspond to those of the amide II band in secondary amides[4)]. In $CH_3CSNHCH_3$ this band is found at 1564 $cm^{-1}$ in the solid state and at 1547 $cm^{-1}$ in the liquid state. On *N*-deuteration, this band moves to a frequency lower by about 30 $cm^{-1}$. Instead of the $\delta$(NH) vibration, the $\delta_a(CH_3)$ vibration couples with the $\nu$(CN) motion in *N*-deuterated species; this gives rise to two frequencies at 1508 and 1438 $cm^{-1}$ in $HCSNDCH_3$. In the case of $CH_3CSNDCH_3$, the $\delta_a(CH_3)_C$[*7] vibration also couples with the $\nu$(CN) vibration, as in the case of $CH_3CSND_2$ (II), the three frequencies are observed at 1515, 1483 and 1442 $cm^{-1}$.

**The Band around 1300 $cm^{-1}$.** — The band at 1297 $cm^{-1}$ of $HCSNHCH_3$ is also assigned to the mixed $\delta$(NH) and $\nu$(CN) vibrations and corresponds to the amide III band of monosubstituted amides. However, the $\delta$(CH) vibration also contributes to this band considerably. Although the spectra of *N*-methylthioacetamides are complicated, it is quite probable that a strong band at 1261 $cm^{-1}$ of the *N*-deuterated species corresponds to the band at 1238 $cm^{-1}$ of $CH_3CSND_2$ (II) in its nature, which is assigned to the composite vibration of skeletal stretching and deformation. In $CH_3CSNHCH_3$ a vibrational interaction certainly takes place between this skeletal and the $\delta$(NH) modes, and the features of the vibration would resemble those of the amide III band. The amide III band occurs at 1299 $cm^{-1}$ in $CH_3CONHCH_3$, which is about 50 $cm^{-1}$ higher than that of $HCONHCH_3$. If we take the above facts into account, the position of the amide III-like band of $CH_3CSNHCH_3$ is estimated at around 1350 $cm^{-1}$ and probably overlaps the $\delta_s(CH_3)_C$ band. This explains the lowering of the band in the carbon tetrchloride solution[*8].

**The Skeletal Stretching Vibrations.**—As has been pointed out in (II), the values of the force constants, $K_{CS}$, $K_{CC}$ and $K_{C'N}$, are close to each other, and interactions occur between the $\nu$(C'N), $\nu$(CS) and $\nu$(CC) vibrations. Therefore, the nature of the observed frequencies in the region from 1100 to 800 $cm^{-1}$ becomes complicated. In addition, the $r(CH_3)_N$ and $r(CH_3)_C$ vibrations are also in this region.

Both (C'N) and $\nu$(CS) vibrations take place in the normal modes of 987 and 868 $cm^{-1}$ of

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[*6] In $HCSNDCH_3$, the bands at ca. 500 and 358 $cm^{-1}$ are assigned, respectively, to the $\pi$(ND) and $\tau$(CN) vibrations.

[*7] In $CH_3CSNHCH_3$, $(CH_3)_C$ and $(CH_3)_N$ are used to refer to the methyl groups attached, respectively, to the carbon and nitrogen atoms.

[*8] The intensity of the band becomes very strong.

HCSNHCH$_3$. The $r$(CH$_3$) vibration also contributes to the former vibration. As for the 868 cm$^{-1}$ band, the energy associated with the $\nu$(CS) vibration is about 55% of the total, and so this band may be called the $\nu$(CS) band. In *N*-deuterated species, the $\delta$(ND) vibration should also be taken into account; the bands at 932 and 844 cm$^{-1}$ are assigned to the mixed vibrations of the $\nu$(C'N) and $\delta$(ND), and of the $\nu$(CS) and $\delta$(ND), respectively.

In CH$_3$CSNHCH$_3$, three strong bands at 1099, 955 and 684 cm$^{-1}$ are assigned to the skeletal stretching vibration. The $r$(CH$_3$)$_N$ vibration may also contribute considerably*[9] to the 1099 cm$^{-1}$ band. The band at 684 cm$^{-1}$ corresponds to the 718 cm$^{-1}$ band of CH$_3$CSNH$_2$ and is certainly associated with the mixed mode of the $\nu$(CS) and $\nu$(CC) vibrations, of which the former is predominant. In *N*-deuterated species, the 956 cm$^{-1}$ band is split into two bands at 990 and 930 cm$^{-1}$; the $\delta$(ND) vibration probably takes place in both of these vibrations.

**The NH Out-of-plane Vibrations.** — The $\pi$(NH) band is termed the amide V band in secondary amides, and can easily be identified by its broadness and sensitivity to a change in states. In secondary thioamides it also occurs at about 680 cm$^{-1}$ in the liquid state and on solidification moves to a frequency higher by about 60 cm$^{-1}$. The $\pi$(ND) band is found at about 500 cm$^{-1}$.

**The Skeletal Deformation Vibrations.**—The band at 600 cm$^{-1}$ of HCSNHCH$_3$ (and of HCSNDCH$_3$) is assigned to one of the skeletal deformation vibrations. The rather high frequency*[10] of the deformation vibration is explained by the vibrational coupling of the $\delta$(NCS) and $\delta$(CNC') modes. In this vibration the N–C=S angle increases while the C–N–C' angle decreases, or vice virsa. In other words, it corresponds to a kind of asymmetrical deformation vibration. Therefore, the band corresponding to the "symmetrical" deformation vibration falls at too low a frequency to be detected.

In CH$_3$CSNHCH$_3$ the bands at 559, 374 and 287 cm$^{-1}$ are assigned to the skeletal deformation vibrations. The 374 cm$^{-1}$ band corresponds to the band at 378 cm$^{-1}$ of CH$_3$CSNH$_2$ and is assigned to the $\delta$(CC') vibration, while the other two are assigned to the "asymmetric" $\delta$(NCS) and $\delta$(CNC') and "symmetric" $\delta$(NCS) and $\delta$(CNC') vibrations respectively.

Thus, the complete assignments of two secondary thioamides, HCSNHCH$_3$*[11] and CH$_3$CSNHCH$_3$, have been made from the calculation of the normal vibrations and from the correspondence of the bands between the related molecules. It has been shown that the assignments of the vibration bands can be made by the trans planar model for the molecules. It has also been shown that the Urey-Bradley force constants so far obtained[1,2,5] have an excellent transferability and can be used without any modification of their values.

The author wishes te express his deep gratitudes to Professor Takehiko Shimanouchi for his guidance and encouragement throughout this work. His thanks are also due to Professor Hidetoshi Takahashi for the use of a PC-1 computer.

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*[9] The band at 1099 cm$^{-1}$ of CH$_3$CSNHCH$_3$ probably corresponds to those around 1100 cm$^{-1}$ of thiolactams which are assigned to the $\nu$(CS) vibration[15].

*[10] The $\delta$(NCS) vibration usually occurs at about 450 cm$^{-1}$ (I), and the $\delta$(CNC'), at 350 cm$^{-1}$ [5].

15) R. Mecke and R. Mecke Jr., *Ber. deut. chem. Ges.*, **89**, 343 (1959).

*[11] In the spectrum of HCSNHCH$_3$, there remain two bands unassigned, e. g. the bands at 467 and 920 cm$^{-1}$. As has been pointed out previously, the vibration associated with the $\delta$(NCS) mode usually occurs about 450 cm$^{-1}$. Like the band around 600 cm$^{-1}$ found in HCONHCH$_3$[5], this band may be assigned to the $\delta$(NCS) vibration of the cis isomer, in which the interaction between the $\delta$(NCS) and $\delta$(CNC') vibrations is considerably weaker than in the trans form.