BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1993—1995(1972)

# Conformations of the Esters. VI.[1] The Conformations of Monothiocarbonates

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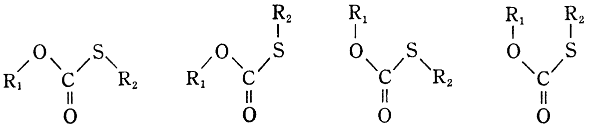
(Received September 3, 1971)

The presence of two or three conformational isomers in monothiocarbonates has been confirmed by nuclear magnetic resonance and infrared spectroscopies and by dipole moment techniques. The data can best be interpreted by assuming that the conformations involving the *s-cis* conformation are more stable than that of *s-trans, s-trans*.

It has been confirmed recently that some formates[2] and carbonates[1] exist as both *s-cis* and *s-trans* conformers with respect to the ester group, and the stability of the two conformational isomers has been discussed. As a natural extension of the study of the conformational analysis of carbonates, the conformations of monothiocarbonates have now been studied.



*s-trans, s-trans* **A** *s-trans, s-cis,* **B** *s-cis, s-trans* **C** *s-cis, s-cis* **D**

Fig. 1. Conformations of monothiocarbonate.

The following conformational isomers of monothiocarbonates may be considered: *s-trans,s-trans* (A), *s-trans, s-cis* (B), *s-cis,s-trans* (C), and *s-cis,s-cis* (D) (Fig. 1). The conformer D is unstable because of the steric repulsion between $R_1$ and $R_2$ groups, although the repulsion should be somewhat smaller in monothiocarbonates than in ordinary carbonates because the C–S bond distance is greater than that of C–O, (C–S, 1.82 Å; C–O, 1.42 Å).[3] Therefore, the conformer D can be neglected.

The chief factors governing the conformations of the ester and the carbonate have been described in previous papers.[1,2] The same factors may be considered for the monothiocarbonates, although there are some points which are different in the monothiocarbonates from the carbonates: 1) the bond moment[4] of the C–S (0.9 D) is a little larger than that of the C–O (0.85 D); 2) the sulfur atom has a larger van der Waals radius (1.85 Å) than oxygen (1.4 Å);[5] 3) the distance of the C–S bond (1.82 Å) is larger than that of the C–O (1.42 Å).

Regarding the first factor, the dipole-dipole interaction between the C=O and the C–S bonds or the C–O and the C–S bonds will be somewhat larger in the monothiocarbonates than in ordinary carbonates (Fig. 2(1)). The second factor necessarily increases the repulsion between sulfur and oxygen in monothiocarbonates, although a part of the repulsion may be released by the third factor. Therefore, the coformer C may be a little more stable than the conformers A and B (Fig. 2(2)). Regarding the third factor, it may be postulated that, in determining the preference of the conformations, the contributions of the steric repulsion between C=O and the $R_2$ group in the conformers A and C, that between $O_{ether}$ and the $R_2$ group in the conformer B, and that between the $R_1$ group and S in the conformer C are smaller in monothiocarbonates than in the carbonates (Fig. 2(3)).

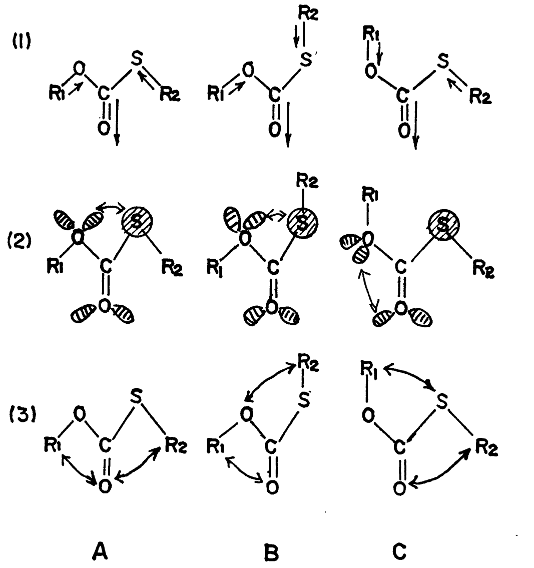


Fig. 2. Factors governing the conformations of monothiocarbonate.

In addition to the above considerations, the sulfur atom may influence the stability of these conformers because its polarizability is larger than that of oxygen.

The purpose of this paper is to present the results of nuclear magnetic resonance and infrared spectral studies and dipole moment measurements undertaken to confirm the existence of conformational isomers in monothiocarbonates.

## Experimental

*Materials.* *General Procedure*: The sodium thiolate, which was prepared by refluxing sodium in thiol and dry ether for several days, was poured into methyl chloroformate in dry ether with ice cooling. The solution was freed from the precipitate, and the monothiocarbonate was distilled.

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[1] Part V: M. Ōki and H. Nakanishi, This Bulletin, **44**, 3419 (1971).

[2] M. Ōki and H. Nakanishi, This Bulletin, **43**, 2558 (1970).

[3] L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," Chemical Society, London (1958).

[4] T. Shimozawa, "Yudenritsu no Kaishaku (Interpretation of Dielectric Constants)," Kyoritsu Shuppan Co., Tokyo (1967).

[5] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca (1967).

*Dimethyl Monothiocarbonate*: bp 63°C/93 mmHg. NMR (τ): $OCH_3$, 6.13; $SCH_3$, 6.34.

S-*Ethyl Methyl Monothiocarbonate*: bp 66—67°C/81 mmHg. NMR (τ): $OCH_3$, 6.12; $C\underline{H}_2CH_3$, 7.07; $CH_2C\underline{H}_3$, 8.62.

S-*Isopropyl Methyl Monothiocarbonate*: bp 50.5°C/20 mmHg. NMR (τ): $OCH_3$, 6.20; $C\underline{H}(CH_3)_2$, 6.53; $CH(C\underline{H}_3)_2$, 8.64.

S-t-*Butyl Methyl Monothiocarbonate*: bp 86—87°C/72 mmHg. NMR (τ): $OCH_3$, 6.25; $C(C\underline{H}_3)_3$, 8.53.

S-*Phenyl Methyl Monothiocarbonate*: bp 125.5°C/20 mmHg. NMR (τ): $OCH_3$, 6.25; aromatic H, 2.60.

Found: C, 57.36; H, 4.66%. Calcd for $C_8H_8O_2S$: C, 57.14; H, 4.80%.

The purities of these compounds were checked by gas chromatography and by studying the infrared spectra and the NMR spectra. The infrared and NMR spectra were measured with the spectrometers previously described.[1] The dipole moment was measured in a benzene solution by the heterodyne beat method.

## Results and Discussion

*Nuclear Magnetic Resonance Spectra.* The NMR spectra of several methyl monothiocarbonates were measured in a carbon tetrachloride solution at room temperature. The results are shown in Table 1. The chemical shifts of the methoxy methyl protons of alkyl methyl monothiocarbonates from TMS change from compound to compound. Since it is difficult to consider that this large shift is due merely to the difference in electronic effects of the alkylthio group, the authors should like to claim that the change is attributable to the change in the population of conformational isomers by the steric effect.

Table 1. NMR spectral data of monothiocarbonates MeOCOSR in $CCl_4$ ($c$=15%)

| | R | $OC\underline{H}_3$ |
|---|---|---|
| I | Me | 6.10$^{(\tau)}$ |
| II | Et | 6.12 |
| III | *i*-Pr | 6.20 |
| IV | *t*-Bu | 6.25 |
| V | Ph | 6.25 |

In order to obtain further information on the existence of conformational isomers, the NMR spectra of *S-t*-butyl methyl monothiocarbonate were measured at low temperatures in $CS_2$–$CH_2Cl_2$. The results are shown in Table 2 and Fig. 3. The peak heights of the methoxy and *t*-butyl protons decrease as the temperature is lowered: the peak height of the methoxy proton at −110°C is 57% of that at 34°C, while that of the *t*-butyl is merely 21% (Fig. 3). These results may best be interpreted by assuming the presence of two or three conformers in this compound and by assuming that the exchange rate among the conformers is slow on the NMR time scale at this low temperature. The broadening both in the peaks of methoxy and *t*-butyl groups may mean the coexistence of three conformers, A, B, and C, or two conformers, B and C, because the chemical shift of the methoxy protons in the conformer A can be considered to be almost the same as that of the conformer B and the same would be true for the chemical shifts of *t*-butyl protons in the conformers A and C, provided that the anisotropic effect of the carbonyl group is the most important in determining the chemical shifts.

Table 2. The intensity change of NMR spectra peaks of *S-t*-butyl methyl carbonate in $CS_2+CH_2Cl_2+$toluene

(The peak area of the methyl signal of toluene added as an internal standard is taken as unity.)

| $T$°C | 34 | −70 | −90 | −100 | −110 | Chemical shift |
|---|---|---|---|---|---|---|
| arom-$\underline{H}$ | 1.32 | 1.38 | 1.37 | 1.41 | 1.68 | 2.77$^{(\tau)}$ |
| arom-$C\underline{H}_3$ | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 7.54 |
| $OC\underline{H}_3$ | 1.60 | 1.36 | 1.21 | 1.00 | 0.91 | 6.23 |
| $C(C\underline{H}_3)_3$ | 4.55 | 3.42 | 2.21 | 1.94 | 0.95 | 8.43 |

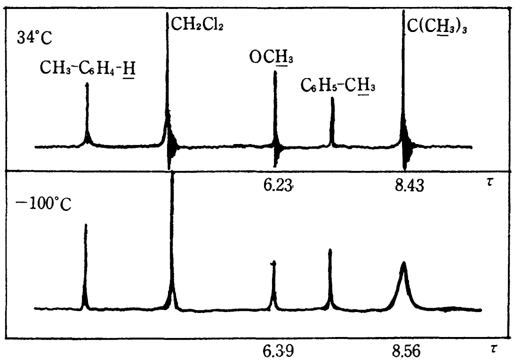
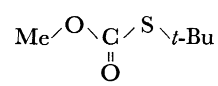
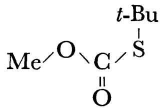


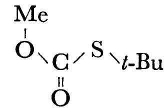
Fig. 3. NMR spectra of MeOCOS-*t*-Bu in $CS_2+CH_2Cl_2+CH_3C_6H_5$.



A



B



C

*Infrared Spectra.* Only a few infrared spectra of carbonyl absorptions of monothiocarbonates have been reported so far;[6,7] only one carbonyl absorption has been reported. However, as was pointed out earlier,[1,2,8] by using an infrared spectrophotometer with a high resolution, we may find two or three carbonyl absorptions for the monothiocarbonates, especially because of the NMR behavior described above. Thus, infrared spectra of carbonyl stretching vibration absorptions of monothiocarbonates were measured in hexane, carbon tetrachloride, and acetonitrile.

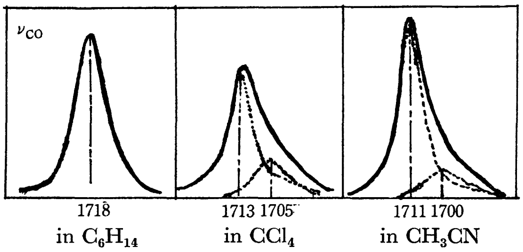


Fig. 4. Carbonyl absorption shapes of *S-t*-butyl methyl monothiocarbonate in three solvents.

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6) R. N. Nyquist and W. J. Patts, *Spectrochim. Acta*, **17**, 679 (1961).

7) A. W. Barker and G. H. Harris, *J. Amer. Chem. Soc.*, **82**, 1923 (1960).

8) M. Ōki and H. Nakanishi, This Bulletin, **44**, 3148 (1971).

Table 3. Carbonyl absorptions of monothiocarbonates $CH_3OCOSR$

| | R | Solvent | | |
|---|---|---|---|---|
| | | $C_6H_{14}$<br>$C=0.02$ mol/$l$<br>cm$^{-1}$ ($\varepsilon$) | $CCl_4$<br>$C=0.0004$ mol/$l$<br>cm$^{-1}$ ($\varepsilon$) | $CH_3CN$<br>$C=0.02$ mol/$l$<br>cm$^{-1}$ ($\varepsilon$) |
| II | Et | 1713 ( 106) | 1707 ( 41) | 1701 ( 91) |
| | | 1720 (1712) | 1715 (600) | 1713 (1065) |
| III | *i*-Pr | 1712 ( 174) | 1705 ( 92) | 1698 ( 114) |
| | | 1718 (2000) | 1714 (787) | 1712 (1050) |
| IV | *t*-Bu | — | 1705 ( 74) | 1700 ( 114) |
| | | | 1713 (739) | 1711 ( 928) |
| V | Ph | 1718 ( 330) | 1711 (112) | 1702 ( 148) |
| | | 1728 ( 64) | 1722 ( 46) | 1715 ( 86) |
| | | 1736 (1711) | 1730 (715) | 1728 ( 918) |

The results confirmed our expectations: monothiocarbonates show unsymmetrical carbonyl absorptions, although the shape of the absorption is not that of the multiple peaks, as is shown in Fig. 4. These unsymmetrical absorptions were graphically separated into two symmetrical peaks.[9] The results are shown in Table 3. With compounds II, III, and IV, the band at a higher frequency is stronger than the lower one in both polar and nonpolar solvents. Apparently in these solvents, the effect of the bulkiness of alkyl groups does not play an important role in determining the conformation of the ester group in contrast to the case of carbonates. From the NMR data, the existing conformers are considered to be B and C or A, B, and C. The directions of the bond dipoles of C=O and C–O or C–S in various conformations suggest that the wave number of the carbonyl absorption of the conformer A is the lowest among the three conformations. However, at the present time, it is not known which of the two conformers, B and C, gives the carbonyl absorption at a higher frequency. Therefore, the most stable conformation cannot be known from the infrared spectral data, although the conformation A is clearly the most unstable.

Compound V has three absorptions in these three solvents, probably indicating that three conformations, A, B, and C, are present. However, since there is a possibility that the third band arises because of the enhancement due to the Fermi resonance, it is necessary to obtain further information. Thus, the infrared spectra of the carbonyl overtone absorptions of *S*-alkyl methyl monothiocarbonate were measured. The results are given in Fig. 5 and Table 4.

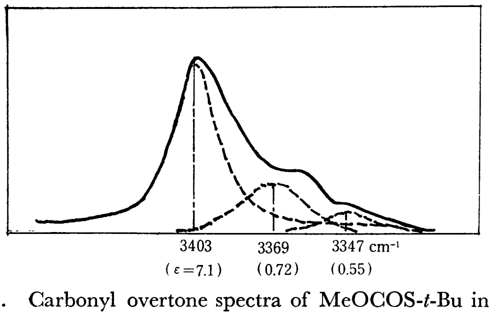

Fig. 5. Carbonyl overtone spectra of MeOCOS-*t*-Bu in $CCl_4$ C=0.0097 mol/*l*.

Table 4. Carbonyl overtone absorptions of monothiocarbonates MeOCOSR in $CCl_4$ $C=0.01$ mol/$l$

| | R | cm$^{-1}$ | ($\varepsilon$) |
|---|---|---|---|
| I | Me | 3388 | (0.41) |
| | | 3397 | (0.34) |
| | | 3416 | (3.81) |
| II | Et | 3362 | (0.20) |
| | | 3380 | (0.36) |
| | | 3409 | (4.51) |
| III | *i*-Pr | 3368 | (0.66) |
| | | 3389 | (1.28) |
| | | 3406 | (4.73) |
| IV | *t*-Bu | 3347 | (0.55) |
| | | 3369 | (0.72) |
| | | 3403 | (7.10) |

The shapes of the absorption curves of compounds I—V are unsymmetrical, and the curves fit best when three rather than two overlapping absorptions are considered.[10] These results strongly suggest that these compounds really show three carbonyl absorptions.

*Dipole Moment.* The temperature dependency of the dipole moment of *S*-*t*-butyl methyl thiocarbonate (IV) was measured in order to obtain information about the stability of these conformers. The results are given in Table 5.

Table 5. Dipole moment of *t*-BuSCOMe in benzene

| *T*°C | 16 | 32 | 53 |
|---|---|---|---|
| (D) | 1.01 | 0.95 | 0.83 |

The calculated dipole moment values of *S*-*t*-butyl methyl monothiocarbonate are 0.1 D for the *s-trans*, *s-trans* conformer (A), 2.1 D for the *s-trans*,*s-cis* conformer (B), and 2.0 D for the *s-cis*,*s-trans* conformer (C).[11] The dipole moment of compound IV decreases as the temperature of the measurement is raised. Since the calculated dipole moment of the conformer B is not very different from that of the conformer C, the results may mean that the *s-trans*,*s-trans* conformer (A) is present, that A is the most unstable, and that the *s-cis* conformers, B and/or C, are the main conformers.

In conclusion, all the data presented above suggest that, among the three possible conformations, the conformation A is the least stable. Thus, although it has not been possible to determine which of the conformations, B and C, is the most stable, it is apparent that the conformations involving the *s-cis* part are more stable than the *s-trans*,*s-trans* conformation. It may be pointed out, as a difference between carbonates and thiocarbonates, that even the simplest example of the latter, dimethyl monothiocarbonate, shows signs of the presence of the three conformers, while the simplest example of the former, ethyl methyl carbonate, gives no such sign.

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[9] The possibility of an absorption including three bands cannot be ruled out. This is especially so when the intensity of the second band is very small and its wave number is close to that of the strong band.

[10] The decomposition of the absorption curves into the component bands is more easily performed in the overtone region because the separation of the components becomes larger.

[11] The calculation was made using the bond moments of 2.4 D for C–O and 0.4 D for C–H. The values for C–O and C–S were cited earlier (See Ref. 4).