The infrared and Raman spectra of methoxycarbonyl and thiomethoxycarbonyl isocyanates

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This paper is dedicated to Professor Gerald W. King on the occasion of his 65th birthday

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The gas phase infrared and liquid phase Raman spectra of the title compounds have been recorded and vibrational analyses performed. The spectra show evidence for the presence in both the liquid and vapour phases of two rotational isomers: *cisoid-Z* and *transoid-Z* with reference to orientation of isocyanato and methyl groups relative to the carbonyl group.

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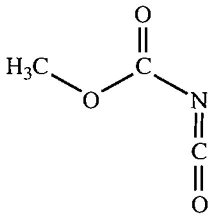
On a enregistré le spectre Raman du composé mentionné dans le titre en phase liquide ainsi que son spectre infrarouge en phase gazeuse et on a effectué des analyses vibrationnelles. Les spectres mettent en évidence, dans la phase liquide et dans la phase gazeuse, l'existence de deux isomères rotationnels : *cisoïde-Z* et *transoïde-Z* en fonction de l'orientation des groupes isocyanato et méthyle par rapport au groupe carbonyle.

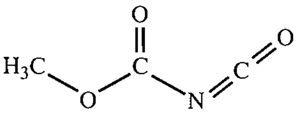
[Traduit par la rédaction]

Introduction

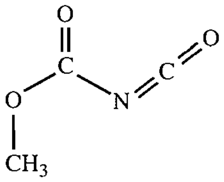
Several papers in recent years have dealt with the infrared and Raman spectra of simple organic isocyanates (1–3). Klapstein and Nau (4) reported infrared, uv, and ^{13}C nmr data for seven carbonyl isocyanates and eight acyl isocyanates and were able to draw a number of general conclusions regarding group frequencies and conformational properties. Their results were subsequently combined with complementary Raman observations to obtain detailed vibrational analyses for acetyl and three chloroacetyl isocyanates (5). The present paper examines the vibrational spectra of the related methoxycarbonyl isocyanate (MCI) and its thio derivative (TMCI). These spectra offer clear evidence for the presence in both liquid and gas phases of more than one rotational conformer. If we neglect rotation of the methyl group and assume a planar molecular framework for the heavy atoms as resonance would favour, there are four isomeric forms to consider, with *cisoid/transoid* and *E/Z* referring to the orientations of the isocyanato and methyl groups, respectively, relative to the carbonyl group:



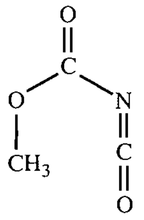
transoid-Z



cisoid-Z



cisoid-E



transoid-E

A detailed analysis of the conformers of MCI, TMCI, and other carbonyl isocyanates has shown that the important contributing structures for MCI and TMCI at room temperature are the *cisoid-Z* and *transoid-Z* conformers (6). In this work we present analyses of the vapour infrared and liquid Raman spectra of MCI and TMCI.

Experimental procedure

Samples of MCI and TMCI were synthesized from commercially available (Aldrich, Milwaukee) chlorocarbonyl isocyanate following the general method of Hagemann (7). The chlorocarbonyl isocyanate was first distilled to remove traces of toluene, indicated to be present as an impurity by ^{13}C nmr, and then converted into the desired methoxy or thiomethoxy compound by reaction with the nucleophiles CH_3OH or CH_3SH, respectively. In the case of MCI, diethyl ether was used as solvent and the primary *N*-carbonyl-substituted carbamoyl chloride was isolated as a white crystalline solid which was then thermally decomposed with elimination of hydrogen chloride to yield product. For the thiomethoxy compound the product was obtained directly following reflux and removal of the 1,2-dichloroethane solvent by distillation. MCI and TMCI are colorless liquids with normal boiling points of 97 and 125°C, respectively.

Infrared spectra of the vapour phase were recorded on a Bruker IFS-25 Fourier transform spectrometer over the range 4000–

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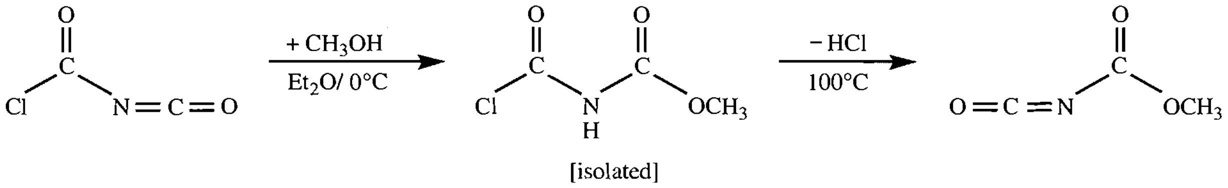
400 cm^{-1}, at a resolution of 2 cm^{-1}. The Raman spectra were measured perpendicular to the incident laser beam on a Jobin–Yvon RAMANOR HG2S monochromator. A Spectra Physics 2020 argon ion laser operating with 500 mW (focussed) power at 514.5 nm was used for excitation. The samples were liquids sealed in glass nmr tubes. Spectra were scanned between 3500 and 100 cm^{-1} and calibrated with reference to chloroform and known argon ion plasma lines. Raman displacements of sharp, unblended features are the average of three independent measurements and have an estimated uncertainty of ±3 cm^{-1}.



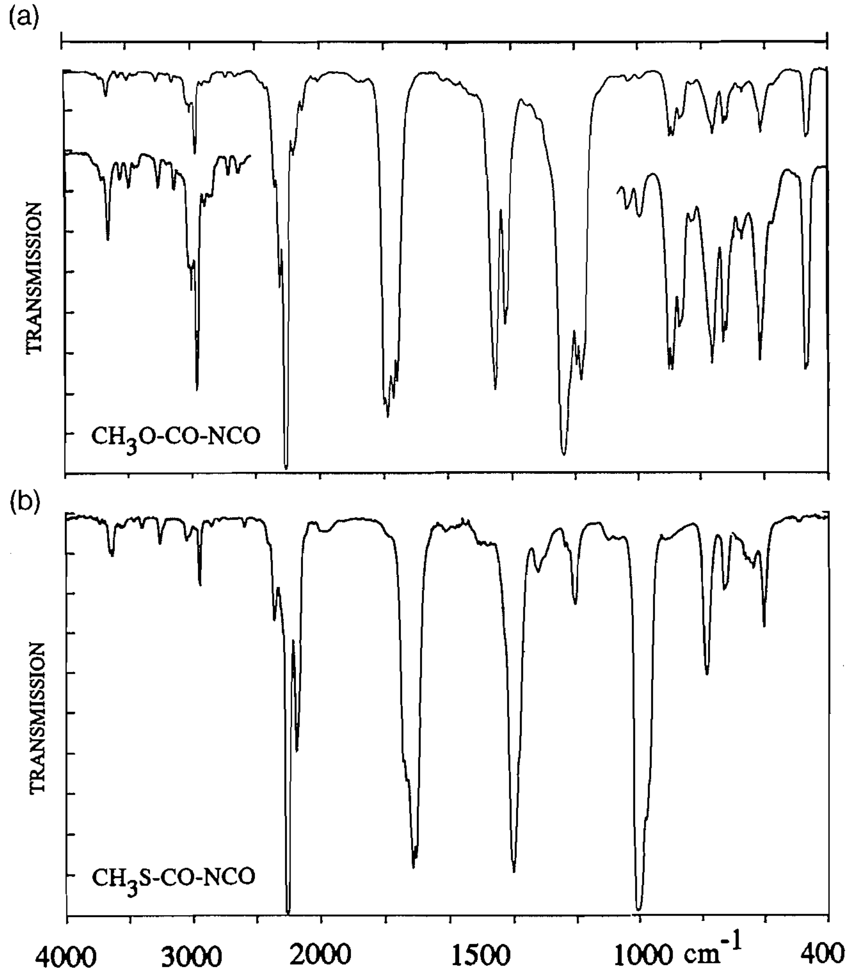


FIG. 1. The vapour phase infrared spectra of MCI and TMCI; (*a*) $CH_3OCONCO$, P = 5 Torr; insert, P = 13 Torr; (*b*) $CH_3SCONCO$, P = 7 Torr.

Results and discussion

MCI and TMCI, in any of the possible planar conformations, can be treated under C_s symmetry, the 24 normal modes spanning the irreducible representations $16a' + 8a''$. All vibrations are both infrared and Raman active. The respective spectra are presented in Figs. 1 and 2. The carbonyl stretching (infrared) region for both compounds is shown in greater detail in Fig. 3 where in each case two absorptions are evident.

A number of observations combine to favour assigning the higher frequency component to the *transoid-Z* conformer and the lower one to the *cisoid-Z* conformer (6). First, the *transoid-E* conformation is clearly improbable for steric reasons. Secondly, the higher frequency component (1795 cm^{-1}) in MCI shows an AB hybrid contour, expected only for the *transoid-Z* isomer. (The *cisoid-Z* and *cisoid-E* isomers should show B-type carbonyl stretching bands.) Thirdly, semi-empirical (AM1) calculations predict a higher frequency for the *transoid-Z* isomer. It is not possible to distinguish between the *cisoid-Z* and *cisoid-E* choices for the lower frequency component (1764 cm^{-1}) solely from observations in the car-

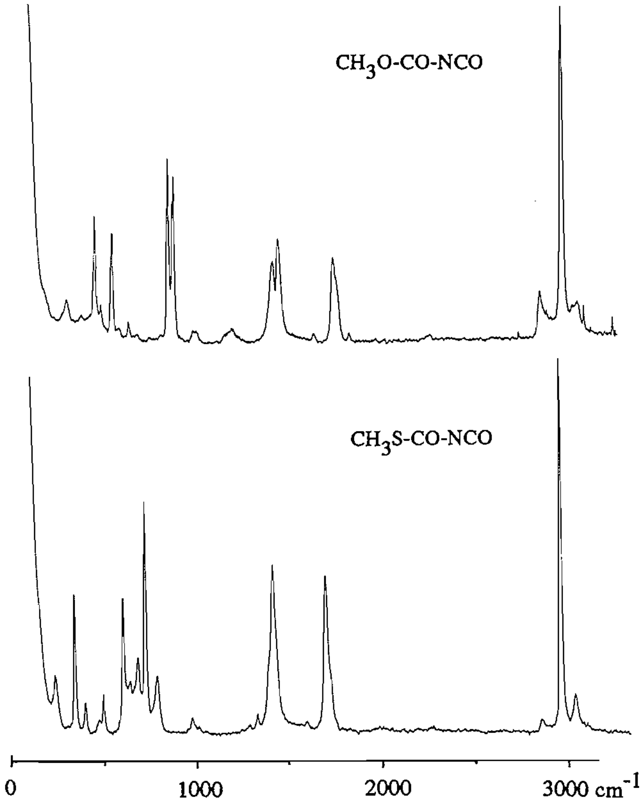


FIG. 2. Raman spectra of MCI and TMCI liquids.

TABLE 1. Observed frequencies (cm^{-1}) and assignments in methoxycarbonyl isocyanate

Infrared vapour	Raman liquid	Assignment
3666 vw		2262 + 1420 = 3682
3504 vvw		2262 + 1235 = 3497
3154 vvw		2262 + 892 = 3154
3036 vvw	3042 mw	$\nu_{as}(CH_3)$; *a′*
3014 vvw	3019 mw	$\nu_{as}(CH_3)$; *a″*
2969 w	2969 vvs	$\nu_s(CH_3)$
2918 vvw		2 × 1454 = 2908
2877 vvw		2262 + 612 = 2874
2856 vvw	2852 mw	2 × 1420 = 2840
2730 vvw		2262 + 466 = 2728
2652 vvw		1764 + 892 = 2656
2346 w		1453 + 892 = 2345
2312 mw		1453 + 862 = 2315
2262 vvs	2250 vw	$\nu_{as}(NCO)$
2201 w		1453 + 763 = 2216
2130 vw		1235 + 892 = 2127
	1834 w	1236 + 604 = 1840
1795 s	1764 ms, sh	$\nu(C{=}O)$ *transoid*
1764 s	1750 ms	$\nu(C{=}O)$ *cisoid*
1453 mw	1456 ms	$\delta_{as}(CH_3)$; $\delta_s(CH_3)$
1420 ms	1424 m	$\nu_s(NCO)$ *cisoid*
1413 ms		$\nu_s(NCO)$ *transoid*
1235 vs	1236 vw	$\nu(C—O)$
1194 s	1196 w	$\rho(CH_3)$; *a′*
1180 s	1171 w	$\rho(CH_3)$; *a″*
	1006 w	$\nu(CH_3—O)$
	993 w	Cℓ—CO—NCO impurity
892 w	896 s	$\nu(C—N)$ *cisoid*
862 w	867 s	$\nu(C—N)$ *transoid*
	821 vw	
763 w	764 vw	$\delta(OCO)$; *a″*
724 w		
	696 vw	
	658 w	$\delta(NCO)$; *a′*
612 w	604 vw	$\delta(NCO)$; *a″*
572 vw	567 ms	$\delta(OCO)$; *a′*
	507 w	321 + 190 = 511
466 w	474 ms	$\delta(OCN)$
	397 vw	2 × 190 = 380
	321 mw	$\delta(COC)$
	~190 vw, sh	$\tau(CH_3)$

bonyl stretching region. However, reference to the C—N stretching region provides a clear distinction. The C—N stretching modes for the two isomers are reasonably well resolved from each other at 892 and 862 cm^{-1} in the infrared spectrum of MCI. Experimentally the 862 cm^{-1} band gains intensity while the 892 cm^{-1} loses intensity upon heating (6). The (scaled) AM1 calculated frequencies are 888 cm^{-1} (*cisoid-Z*), 867 cm^{-1} (*transoid-Z*), and 852 cm^{-1} (*cisoid-E*). One can thus confidently assign the 862 cm^{-1} band to the *transoid-Z* isomer, with the second isomer being the *cisoid-Z* form. The temperature dependence of the 862 cm^{-1} band parallels that of the 1795 cm^{-1} carbonyl band, while the behaviour of the 892 cm^{-1} band follows that of the 1764 cm^{-1} carbonyl band. This allows unambiguous assignment of the two conformers of MCI as *transoid-Z* and *cisoid-Z*, with the latter being the more stable (6). Similar arguments hold for TMCI, allowing some conformeric vibrational assignments (see Table 2).

Vibrations of the methyl group

The stretching vibrations for a methyl group, whether attached to an oxygen atom or to a sulphur, are found in the 3050–2900 cm^{-1} region. Their assignments follow directly from the expectation that the symmetric mode will give the most intense Raman line in the region and that the frequencies of the two asymmetric counterparts will have frequencies similar to one another and lie slightly higher than the symmetric mode. The deformation modes can be assigned by comparison to methyl (8) and thiocarbamate (9) esters. The symmetric deformation lies typically near 1450 cm^{-1} for the $CH_3—O$ group and 1320 cm^{-1} for the $CH_3—S$ group (10). In the spectra of MCI and TMCI it is probable that the symmetric and asymmetric deformations are nearly degenerate as only one frequency attributable to CH_3 deformation can be identified. Infrared bands at 1194 and 1180 cm^{-1} have been assigned to the *a′* and *a″* $CH_3—O$ rocking modes. The corresponding frequencies for $CH_3—S$, since these modes are mass-sensitive, are anticipated to be lower, e.g., 968 cm^{-1} is observed in $CH_3S—CO—NH_2$ (9), and a vibration with 973ir/965R cm^{-1} is assigned to the $CH_3—S$ rocking motion.

NCO stretching vibrations

A strong infrared absorption in the 2280–2250 cm^{-1} region is characteristic of the isocyanate functional group. As with other organic isocyanates that we have studied, this asymmetric NCO stretch appears only weakly in the Raman spectra. On the other hand, the corresponding symmetric motion leads to rather weak ir absorption but intense Raman activity. These generalizations allow unambiguous assignments to be made for ν_{as} (NCO) and ν_s(NCO).

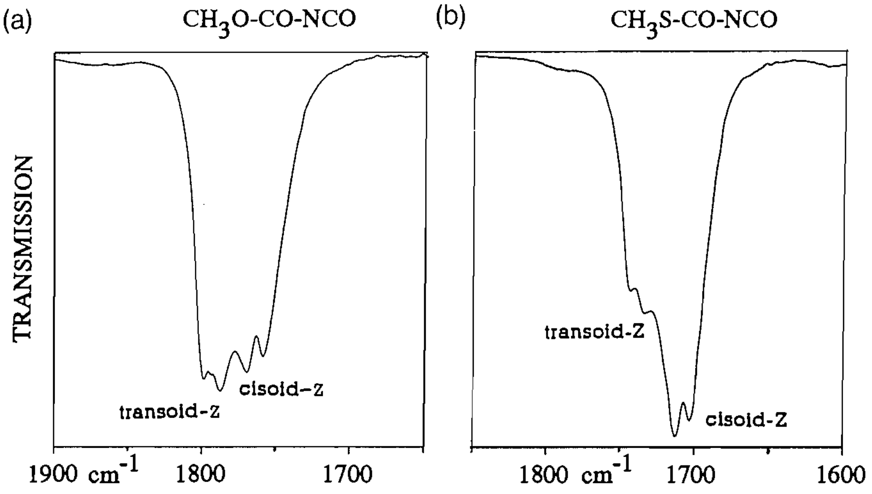


FIG. 3. The carbonyl stretching region in the infrared spectra of MCI and TMCI.

TABLE 2. Observed frequencies (cm^{-1}) and assignments in thiomethoxycarbonyl isocyanate

Infrared vapour	Raman liquid	Assignment
3653 vw		2257 + 1404 = 3661
3635 vw		2257 + 1384 = 3641
3462 vvw		2257 + 1208 = 3465
3394 vvw		2 × 1709 = 3418
3255 vvw		2257 + 1004 = 3261
3046 vvw		$\nu_{as}(CH_3)$; *a′*
3023 vvw	3021 m	$\nu_{as}(CH_3)$; *a″*
2945 w	2940 vvs	$\nu_s(CH_3)$
2850 vvw	2835 mw	
2360 mw		
2257 vvs	2241 vvw	$\nu_{as}(NCO)$
2187 w		1404 + 787 = 2191
2177 vw, sh		1384 + 787 = 2171
1836 vvw		
1740 ms	1711 ms, sh	$\nu(C{=}O)$ *transoid*
1709 s	1689 s	$\nu(C{=}O)$ *cisoid*
	1585 w	2 × 786 = 1572
1404 s	1407 s	$\nu_s(NCO)$ *cisoid*
1384 m, sh	1385 ms, sh	$\nu_s(NCO)$ *transoid*
1323 w	1319 mw	$\delta_s(CH_3)$
1270 vvw	1265 w	2 × 637 = 1274
	1231 vvw	637 + 604 = 1241
1208 w		
1004 vs	1001 vvw	$\nu(C{-}N)$ *cisoid*
973 s, sh	965 vw	$\rho(CH_3)$; $\nu(C{-}N)$ *transoid*
787 m	786 m	
727 mw	725 vs	$\nu(C{-}S)$
689 vw	684 m	$\nu(CH_3{-}S)$
639 vvw	637 mw	$\delta(NCO)$; *a′*
606 mw	604 ms	$\delta(NCO)$; *a″*
490 vvw	498 w	$\delta(OCS)$
	470 vw	2 × 240 = 480
	403 w	2 × 202 = 404
	346 ms	$\delta(S{-}C{-}N)$
	240 mw	$\delta(CSC)$
	~202 w, sh	$\tau(CH_3)$

CH_3—O and CH_3—S stretching vibrations

The infrared spectrum of MCI shows nothing of great significance in the region between 1180 and 900 cm^{-1} where methoxy C—O stretching frequencies are to be expected. A weak Raman line at 1006 cm^{-1} is tentatively attributed to this mode. The corresponding C—S stretch in TMCI can be assigned with more confidence to a moderately intense Raman feature at 684 cm^{-1}. Again the corresponding infrared absorption is very weak. The mode is reported at 696 cm^{-1} in CH_3S—CO—NH_2 (9) and 692 cm^{-1} in CH_3—S—CH_3 (10). The adjacent bonds, from O or S to the carbonyl group, are somewhat stronger through resonance than are those to the methyl group, and this is reflected in somewhat higher values for the associated stretching frequencies: 1235 cm^{-1} for MCI and 727 cm^{-1} for TMCI.

Skeletal bending vibrations

The COC/CSC deformation mode lies at 321 and 240 cm^{-1} in MCI and TMCI, respectively. They represent the lowest frequency motions identified in the spectra, with the possible exception of poorly resolved shoulders on the rising Rayleigh scattered background, which may be due to the methyl torsion. The CNC bends are also expected to be low-lying but probably have frequencies below 150 cm^{-1}. The δ(COC/CSC) values may be compared with 320 and 253 cm^{-1} found for the analogous carbamates (9, 11). Bending vibrations within the C—NCO group can be assigned with reference to other organic isocyanates (6).

Observations and their assignments are listed for MCI and TMCI in Tables 1 and 2, respectively.

Acknowledgments

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1. S.E. Ulic, C.O. Della Védova, and P.J. Aymonino. J. Raman Spectrosc. **21**, 283 (1990).
2. J.F. Sullivan, S.K. Nandy, M.J. Lee, and J.R. Durig. J. Mol. Struct. **266**, 271 (1992).
3. J.F. Sullivan, S.K. Nandy, M.J. Lee, and J.R. Durig. J. Raman Spectrosc. **23**, 51 (1992).
4. D. Klapstein and W.M. Nau. Spectrochim. Acta. In press.
5. W.J. Balfour, S.G. Fougère, D. Klapstein, and W.M. Nau. J. Mol. Struct. In press.
6. D. Klapstein and W.M. Nau. J. Mol. Struct. In press.
7. H. Hagemann. Angew. Chem. Int. Ed. Engl. **16**, 743 (1977).
8. J.K. Wilmshurst. J. Mol. Spectrosc. **1**, 201 (1957).
9. Lin Z., R. Mattes, H. Schnöckel, M. Thünemann, E. Hunting, U. Höhnke, and Ch. Mendel. J. Mol. Struct. **117**, 117 (1984).
10. M. Tranquille, P. Labarbe, M. Fouassier, and M.T. Forel. J. Mol. Struct. **8**, 273 (1971).
11. J.C. Carter and J.E. Devia. Spectrochim. Acta, **29A**, 623 (1973).