

# THE INFRARED SPECTRA OF A QUATERNARY THIOCYANIDE

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## ABSTRACT

The infrared spectra of 1-methylthio-1-dimethylamino methyl cyanide in tetrachloromethane and its S-methyl deuterated derivative were measured in trichloromethane solvents. The presence of at least, a *trans* and a *gauche* rotamer in trichloromethane solution and a *gauche* rotamer in the tetrachloromethane is suggested. Also, the enormous enhancement of the cyanide band intensity in the  $-SCD_3$  derivative was recorded. For the *trans* isomer, the intensity enhancement is attributed to resonance coupling interaction between the cyanide stretch and the  $CD_3$  asymmetric stretch due to first order Coriolis and second order centrifugal distortion perturbations.

## INTRODUCTION

Dessey and Poivre<sup>1</sup> analysed the vibrational spectra of thiocyanodimethylamide some twenty years ago. However, the related quaternary cyanides which concern us now have interesting structural features which are different from the parent compounds. One of these quaternary compounds, 1-methylthio-1-dimethylamino methyl cyanide (I) has one chiral centre and two potential centres of rotational isomerism. If in considering the possible rotamers only rotation about the  $CH_3S-C$  bond is taken into account there is possibility of, at least, one *trans* and two *gauche* forms (Fig. 1). Because of the bulk of the  $NMe_2$  substituent only one (*gauche* I) of the two *gauche* forms is likely.

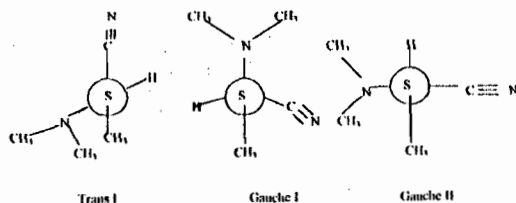


Fig. 1. Rotamers of 1-Methylthio-1-Dimethylamino Methylcyanide

Preliminary survey<sup>2</sup> of the infrared spectra of (I), 1-methyl-1-4-morpholinobenzylcyanide, p-chloro-1-methylthio-1-4-morpholinobenzyl cyanide in trichloromethane and tetrachloromethane solutions showed interesting solvent effects on the cyanide band. We now report a more detailed study of the infrared spectra of (I).

## EXPERIMENTAL

### Preparation of samples

(I) was prepared according to Okecha's procedure<sup>3</sup> and, the S - methyl deuterated derivative obtained

by methylating with deuterio-methyl iodide in place of methyl iodide. The deuteration was meant to distinguish the methyl vibrations of S-Me from those of N-Me<sub>2</sub>.

### Infrared spectra measurements

Infrared spectra were recorded in the region 4000 to 667  $cm^{-1}$  with a Pye - Unicam SP 1200 double beam spectrophotometer. Samples were in tetrachloromethane and trichloromethane solutions at concentrations not exceeding 0.5 mole  $dm^{-3}$ .

## RESULTS AND DISCUSSION

Table 1A. Infrared bands ( $cm^{-1}$ ) of 1-methylthio-1-dimethylamino methylcyanide (RSCN<sub>3</sub> and (RSCD<sub>3</sub>) in  $CCl_4$  solution

RSCN <sub>3</sub>	RSCD <sub>3</sub>	Assignment
2954	2954	comb. 1408 + 1460(A <sup>+</sup> )
2924	2923	fund. C(4,5) H <sub>3</sub> sym. str. (A <sup>+</sup> ) and
2899	2118	fund. C(3)H <sub>3</sub> (2899) sym. str. (A <sup>+</sup> ) and C(3)D <sub>3</sub> (2118) sym. str. (A <sup>+</sup> )
2844	2843	overtone 2 x 1420, C(4,5) H <sub>3</sub> sym. def. (A <sup>+</sup> )
2809	2810	overtone 2 x 1408
2764	2766	overtone 2 x 1360, C(4,5)H <sub>3</sub> sym. def. (A <sup>+</sup> )
2227	2228	fund. C(1)N str. (A <sup>+</sup> )
	2215	
1680	1686	fund. C(2)-N str. coupled (A <sup>+</sup> ) or
1675	1681	overtone 2 x 835
1465	1468	fund. C(4,5)H <sub>3</sub> def. + C(4,5)H <sub>3</sub> rocking or C(4,5)H <sub>3</sub> def. (A <sup>+</sup> )
1455	1460	fund. C(4,5)H <sub>3</sub> def. + C(4,5)H <sub>3</sub> rocking or C(4,5)H <sub>3</sub> def. (A <sup>+</sup> )
1450	1454	fund. C(4,5)H <sub>3</sub> asym. def. (A <sup>+</sup> )
1435	1049	fund. C(3)H <sub>3</sub> (1435) asym. def. (A <sup>+</sup> ) and C(3)D <sub>3</sub> (1049) asym. def. (A <sup>+</sup> )
1430	1049	fund. C(3)H <sub>3</sub> (1435) asym. def. (A <sup>+</sup> ) and C(3)D <sub>3</sub> (1049) asym. def. (A <sup>+</sup> )
1405	1408	fund. C(4,5)H <sub>3</sub> sym. def. (A <sup>+</sup> )
1380	1011	fund. C(3)H <sub>3</sub> (1380) sym. def. (A <sup>+</sup> ) and C(3)D <sub>3</sub> (1011) sym. def. (A <sup>+</sup> )
1330	1338	fund. C(2)-H def.
1275	1278	fund. R'NC <sub>2</sub> skeleton, asym. str. (A <sup>+</sup> )
1258	1263	fund. C(4,5)H <sub>3</sub> rocking (A <sup>+</sup> ) + R'NC <sub>2</sub> asym. str. (A <sup>+</sup> )
1212	1218	fund. C(4,5)H <sub>3</sub> rocking + (A <sup>+</sup> )
1161	1162	fund. C(4,5)H <sub>3</sub> rocking + (A <sup>+</sup> )
1090	1101	fund. C(4,5)H <sub>3</sub> rocking + (A <sup>+</sup> )
1049	1048	fund. C(4,5)H <sub>3</sub> rocking (A <sup>+</sup> )
1026	1026	fund. C(2)-N str. (A <sup>+</sup> )
979	906	fund. C(3)H <sub>3</sub> rocking + C(2)-C(1) str + C(2)-S str. (979) and C(3)D <sub>3</sub> (906) def. + C(3)H <sub>3</sub> (966) def. and C(3)D <sub>3</sub> (841) def.
899	697	fund. C(3)-S-C(2) str.
834	836	fund. R'NC <sub>2</sub> sym. str. or C-CN str.
674	671	fund. C-S str. (A <sup>+</sup> )

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Table 1B. Infrared bands ( $\text{cm}^{-1}$ ) of 1-methylthio-1-dimethylamino methylecyanide ( $\text{RSCN}_2$ ) and ( $\text{RSCD}_2$ ) in  $\text{CHCl}_3$  solution

$\text{RSCN}_2$	$\text{RSCD}_2$		Assignments
2999	2997	fund.	C(2)-H str. ( $A'$ ) or C(4,5)H <sub>2</sub> asym. str. 1408 + 1460 ( $A''$ )
2960	2957	comb.	
2960	2923	fund.	C(4)H <sub>2</sub> , C(5)H <sub>2</sub> sym. str. ( $A''$ )
2930	2116	fund.	C(3)H <sub>2</sub> sym. str. ( $A''$ ), C(3)D <sub>2</sub> sym. str. ( $A''$ )
2845	2843	overtone	2 x 1420, C(4,5)H <sub>2</sub> sym. def. ( $A''$ )
2815	2810	overtone	2 x 1408
2770	2767	overtone	2 x 1380, C(4,5)H <sub>2</sub> sym. def. ( $A''$ )
2231	2227	fund.	C(1)N str. ( $A''$ )
2215	2215		
1673	1673	fund. or overtone	C(2)-N str. coupled ( $A'$ ) 2 x 835
1468	1468	fund.	mainly C(4,5)H <sub>2</sub> def. + C(4,5)H <sub>2</sub> rocking
1461	1461	fund.	mainly C(4,5)H <sub>2</sub> def. + C(4,5)H <sub>2</sub> rocking or C(4,5)H <sub>2</sub> def. ( $A''$ )
1454	1454	fund.	C(4,5)H <sub>2</sub> asym. def. ( $A''$ )
1438	1052	fund.	C(3)H <sub>2</sub> (1438) asym. def. ( $A'$ ) and C(3)D <sub>2</sub> (1052) asym. def. ( $A'$ )
1435	1052	fund.	C(3)H <sub>2</sub> (1438) asym. def. ( $A'$ ) and C(3)D <sub>2</sub> (1052) asym. def. ( $A'$ )
1408	1408	fund.	C(4,5)H <sub>2</sub> sym. def. ( $A''$ )/CH def.?
1388	1388	fund.	C(4,5)H <sub>2</sub> sym. def. ( $A''$ )
1279	1281	fund.	R'NC <sub>2</sub> asym. str. ( $A''$ )
1256	1265	fund.	C(4,5)H <sub>2</sub> rocking ( $A''$ )
1229	1230	fund.	Me <sub>2</sub> N asym. str. + rocking C(4,5)H <sub>2</sub> ( $A''$ )
1166	1164	fund.	C(4,5)H <sub>2</sub> rocking ( $A''$ )
1099	1103	fund.	C(4,5)H <sub>2</sub> rocking ( $A''$ )
1052	1050	fund.	C(4,5)H <sub>2</sub> rocking ( $A''$ )
1030	1029	fund.	C(2)-N str. ( $A'$ )
	1014	fund.	C(3)D <sub>2</sub> def.
982	901	fund.	C(3)H <sub>2</sub> (982) and C(2)D <sub>2</sub> (901) rocking + C(2)-C(1) str.
967	846	fund.	C(3)H <sub>2</sub> (967) rocking and C(3)D <sub>2</sub> (846) def.
898	699	fund.	C(3)-S-C(2) str.
836	835	fund.	R'NC <sub>2</sub> sym. str. ( $A''$ ) or C-CN str. + ....
677	671	fund.	C-S str. ( $A'$ )
	636		

Table 1(A,B) summarises the results. The peak positions ( $\text{cm}^{-1}$ ) are listed together with tentative band assignments. The band positions did not change significantly with concentration between 0.2 and 0.5 mole  $\text{dm}^{-3}$  but considerable band overlap occurred expectedly in each of the regions, 3000; 1500 - 1300; 1300 - 700  $\text{cm}^{-1}$

### 3000 $\text{cm}^{-1}$ region

The trans and gauche rotamers have the same spectrum in this region. Nine possible  $\text{CH}_3$ -stretching fundamentals are expected with considerable band overlap. The estimated positions of the 2999, 2954, 2900  $\text{cm}^{-1}$  peaks on S-Me deuteration are 2205, 2172 and 2132  $\text{cm}^{-1}$  respectively. Apparently, only the 2900  $\text{cm}^{-1}$  peak suffered an isotopic shift with a  $v_{\text{CH}}/v_{\text{CD}}$  ratio of 1.57, suggesting that this band is due to a S-methyl vibration almost free from coupling with other vibrations, that all other bands due to the methyl vibrations in the S-Me are of low intensity, and that all the other bands in this region except the one near 2900  $\text{cm}^{-1}$  are due to methyl vibrations of  $\text{NMe}_2$ .

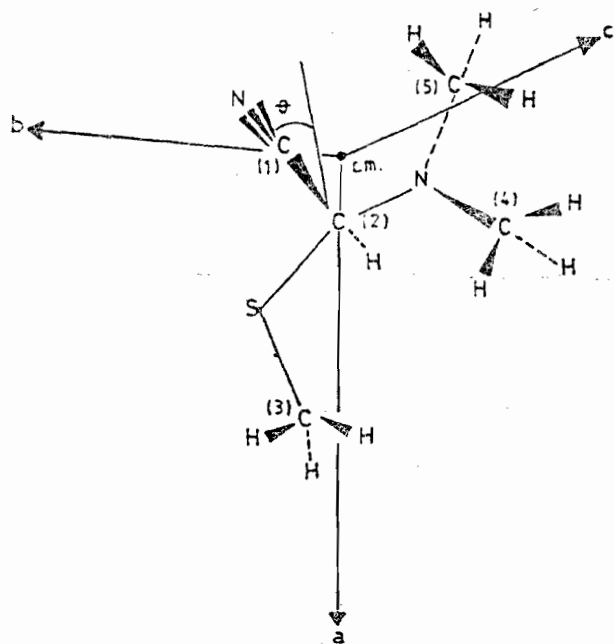
### 1700 - 1400 $\text{cm}^{-1}$ region

There is, apparently, no clean band in this region. Near the 1400  $\text{cm}^{-1}$  end there are six peaks to be

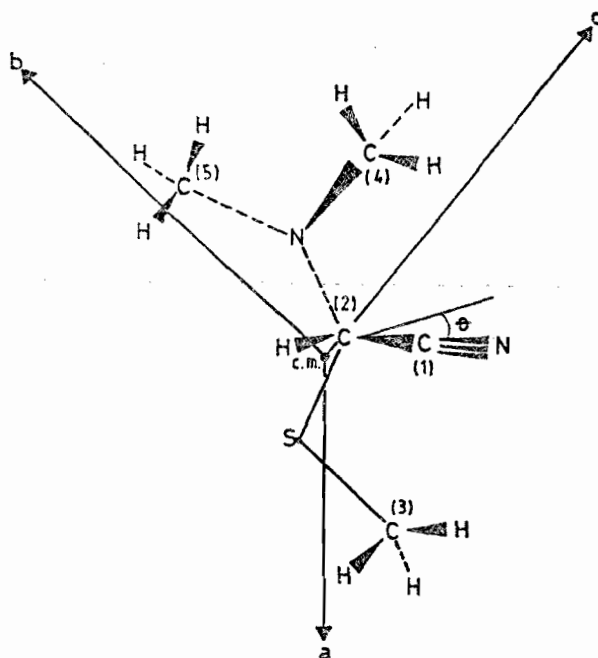
accounted for. One of these, the 1450  $\text{cm}^{-1}$  peak will be taken up later. On S-methyl deuteration, the doublet near 1430  $\text{cm}^{-1}$  which almost completely disappears and is presumed shifted to near 1050  $\text{cm}^{-1}$  has a component which is almost certainly the asymmetric methyl deformation mode of methyl in S-Me group. The  $v_{\text{H}}/v_{\text{D}}$  ratio for this mode is about 1.41 - very little coupling with other vibrations probably. The other component of the same doublet is near 1435  $\text{cm}^{-1}$  and, by analogy with the spectra of  $\text{CH}_3\text{SCD}_2\text{CD}_3$  and methyl isopropyl sulphide, is attributed to another asymmetric methyl deformation of  $\text{SMe}^{5,7}$ . At the other end of the region is the doublet near 1680  $\text{cm}^{-1}$  which, on S-Me deuteration, suffers a drastic peak height reduction without a significant shift in position or change in shape. Beside the overall intensity reduction, the higher frequency component suffers an apparent relative solvent red shift and intensity enhancement from trichloromethane to tetrachloromethane.

We attempt a tentative assignment of the 1680  $\text{cm}^{-1}$  band on the basis of comparison with the spectra of other quaternary cyanides. The series R.Y.CCN (II R =  $\text{C}_6\text{H}_5\text{Me}_2\text{N}$ ; III R =  $-\text{XCH}_3$ ; IV R =  $\text{C}_6\text{H}_5\text{CH}_2\text{X}$ ; V R =  $\text{C}_6\text{H}_5\text{X}$ ; VI R =  $p\text{-ClC}_6\text{H}_4\text{X}$ ; VII R =  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{XMe}_2\text{CHS}$ ; Y =  $-\text{SCH}_3$ ; X =  $-\text{NC}_4\text{H}_8\text{O}$ ), show<sup>3</sup>, in *nujol*, a peak near 1600  $\text{cm}^{-1}$  which we take to be of the same origin as the 1680  $\text{cm}^{-1}$  peak. We note that in these quaternary cyanides, the 1600  $\text{cm}^{-1}$  suffers only minimal shift in position in spite of the changes in substituents. On the other hand, the C-NC<sub>2</sub> skeleton of C-NMe<sub>2</sub>, i.e. C-NRR<sub>2</sub>, is common to all. We infer that the dominant vibration responsible for the 1600  $\text{cm}^{-1}$  is within the C-NC<sub>2</sub> skeleton in most of these molecules. The position in (V) (1580  $\text{cm}^{-1}$ ) as compared with 1640  $\text{cm}^{-1}$  in II suggests that the shifts away from 1600  $\text{cm}^{-1}$  are probably indicators of mainly electronic substituent effects (or force constant changes) rather than mass effects. In particular, the shift in the morpholino derivative, II, appears to be from a different source - coupling with the C-CH<sub>3</sub> stretch.

The 1680  $\text{cm}^{-1}$  band in (I) is attributed to a similar origin namely, that it is a C-NMe<sub>2</sub> stretch coupled with the C-H bend of the hydrogen of the tertiary carbon. This assignment is plausible when we note that the 1542  $\text{cm}^{-1}$  band of  $\text{NC.CSeNMe}_2$ , the 1560  $\text{cm}^{-1}$  band of  $\text{HCO.NMe}_2$  and the 1536  $\text{cm}^{-1}$  band of  $\text{NC.CO.NMe}_2$  are all assigned to the C-NMe<sub>2</sub> stretch coupled to various other vibrations. The expected enhancement of the frequency of this stretching vibration in the thioformamides, on S-methylation, is observed in our S-methyl derivative. Alternatively, it (the 1680  $\text{cm}^{-1}$  band) may be



TRANS-STRUCTURE OF  $\text{Me}_2\text{NCH}(\text{SMe})\cdot\text{C}\equiv\text{N}$



GAUCHE (I) STRUCTURE OF  $\text{Me}_2\text{NCH}(\text{SMe})\cdot\text{C}\equiv\text{N}$

Fig. 2. Principal rotational axes of trans and gauche (I) rotamers of  $\text{Me}_2\text{NCH}(\text{SMe})\cdot\text{C}\equiv\text{N}$

assigned to the first overtone of the  $835\text{ cm}^{-1}$  band.

#### 1400 - 800 $\text{cm}^{-1}$ region

One of the three methyl deformation bands ( $1430\text{ cm}^{-1}$ ) of the same group having been assigned, two more are expected. On S-methyl deuteration, the intensity of the peaks at  $1450$  and  $1380\text{ cm}^{-1}$  drops considerably, but not to zero, without any changes in shape. In addition, a new band is recorded at  $1011\text{ cm}^{-1}$ . The spectra of dimethylamino compounds show two bands near  $1400\text{ cm}^{-1}$  and the methyl deformation vibration frequency usually occurs above  $1400\text{ cm}^{-1}$ . Accordingly, we attribute the  $1405\text{ cm}^{-1}$  band of (I) to the methyl deformation vibration of  $\text{NMe}_2$ . The  $1380\text{ cm}^{-1}$  peak is taken as a superposition of two bands, one due to a methyl deformation vibration of  $\text{SMe}$  and the other is, more or less, of the same type of vibration, but of the  $\text{NMe}_2$ .

The peak near  $1011\text{ cm}^{-1}$  is attributed to the  $\text{CD}_3$  deformation of  $\text{SCD}_3$  arising from the isotopic shift of the  $1380\text{ cm}^{-1}$  band, giving  $\nu_{\text{H}}/\nu_{\text{D}}$  ratio of 1.4.

There is solvent sensitive peak near  $1212\text{ cm}^{-1}$  in tetrachloromethane. The spectra of  $\text{NC}\cdot\text{CSNMe}_2$ ,  $\text{HCDNMe}_2$  and the dimethylamino phenols in this region suggest that this band is due to the asymmetric stretch of the dimethylamino skeleton.

#### 700 $\text{cm}^{-1}$ region

Two bands are recorded near  $712$  and  $675\text{ cm}^{-1}$  in tetrachloromethane and one ( $675\text{ cm}^{-1}$ ) in

trichloromethane. To assign these bands, one notes some features of the spectra of methyl isopropyl sulphide. There are three or four bands ( $725$ ,  $690$ ,  $637$ ,  $610\text{ cm}^{-1}$ ) observed in this region in the liquid and two ( $725$ ,  $637\text{ cm}^{-1}$ ) in the solid. In the sulphide all three bands of the liquid spectra have been assigned to a C-S stretching mode, and we suppose the  $712$  and  $675\text{ cm}^{-1}$  bands of the present spectra to correspond respectively to the  $725$  and  $637\text{ cm}^{-1}$  bands of the sulphide. On S-methyl deuteration of our compound (I), three or more bands are recorded in each solvent so that the number of bands in trichloromethane is apparently more.

The  $675\text{ cm}^{-1}$  band is not affected by deuteration; an additional band shows up in trichloromethane which is also observed in tetrachloromethane at  $655\text{ cm}^{-1}$ , and there is another close to  $700\text{ cm}^{-1}$  in both solvents.

#### Trans - gauche preponderance

There are two features of the spectra of (I) that are of some interest: the occurrence of conformational bands and the enhancement of the intensity of the cyanide band in the deuterated S-methyl analogue of (I).

In the infrared and Raman spectra of alkylsulphides, the  $\text{CH}_3\text{-S}$  stretching bands provide a basis for the identification of the trans and gauche rotamers in the liquids and solids<sup>7,8</sup>. As already noted, similar bands are also observed in (I) and may serve the

same purpose. Accordingly, we suggest that the presence of a peak at  $675\text{ cm}^{-1}$  is an indication of the preponderance of the trans rotamer in both tri- and tetrachloromethane solutions. Because the  $712\text{ cm}^{-1}$  peak occurs in tetrachloromethane solution only, the gauche rotamer may be more stable in that solution than in trichloromethane.

#### *The cyanide band intensity*

The results of Thompson's measurements<sup>9</sup> of the spectra of cyanides show that  $\text{NMe}_2$  substitution on alpha carbon lowers the frequency of the cyanide vibration. Thus a cyanide peak of  $2232\text{ cm}^{-1}$  for diethylamino cyanomethane in tetrachloromethane solution is reported as compared with  $2227\text{ cm}^{-1}$  for (I). But the intensity of the same band, which is measurable in the former compound, is too weak to be observed in (I) and enhanced considerably on S-methyl deuteration without any shift in peak position. The indications are that the substituent effect, not intensity, of the dimethylamino group is dominant in determining the peak position in these compounds and (I).

#### *Resonance in S-methyl deuterated I*

The deuteromethyl stretching frequency of  $\text{SCD}_3$  is within  $200\text{ cm}^{-1}$  of the cyanide peak position and a resonance of some sort is expected, one in which Coriolis interaction or centrifugal perturbations lead to the *borrowing* of intensity from the  $\text{CD}_3$  stretching band by the CN stretch to enhance the intensity of the latter.

If intensity *borrowing* is due to a Coriolis type resonance, rotation of suitable symmetry is required. For this purpose, we have calculated the rotational constants for one trans and the gauche (I) rotamers. The trans isomer gives  $A = 0.002$ ,  $B = 0.060$ ,  $C = 0.16\text{ cm}^{-1}$  with an asymmetry parameter  $K = 0.91$  while for the gauche (I) structure,  $A = 0.104$ ,  $B = 0.088$ ,  $C = 0.070\text{ cm}^{-1}$  and  $K = 0.10$ . Thus the former is an oblate top while the latter is strongly asymmetric top. For convenience, only the oblate top-trans will be considered.

Next we take  $C_s$  as the approximate point group of the oblate top with the CSCN skeleton as a near

symmetry plane,  $\text{NC}_2$  plane of  $\text{NMe}_2$  perpendicular to the symmetry plane and CN in the plane of symmetry (Fig. 2). The cyanide stretch then belongs to the  $A'$  Symmetry specie as does the  $\text{CD}_3$  symmetric stretch, but the  $\text{CD}_3$  asymmetric stretch is of  $A''$  specie.

With the assumption that the most important component of the dipole moment is in the plane of symmetry, the nitrile stretching mode is coupled with the  $\text{CD}_3$  asymmetric stretch through first-order Coriolis and or second order centrifugal distortion interaction by rotation about the a or b axis. If there is a significant contribution of CN to the z-component of the dipole moment, then some Coriolis coupling with the symmetric stretch of  $\text{CD}_3$  is also possible.

As to the sensitivity of the CN stretching frequency to these resonance perturbations, it is readily shown that if the separation between the harmonic frequencies of the CN and  $\text{CD}_3$  stretching modes are small to second order with respect to the perturbation matrix element, between the two modes, the cyanide peak position may not shift significantly in spite of intensity *borrowing*.

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