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Conformational Characterization of *S*-Methyl Dithiocarbazate by Infrared Spectra and Vibrational Assignments

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Infrared spectra are recorded for *S*-methyl dithiocarbazate and its *N*-deuterated compound in two molecular conformations in the solid state and in solution between 4000 and 30 cm^{-1}. The assignments have been supported from a complete normal coordinate analysis; the conformation sensitive bands of the $-CSNHNH_2$ grouping are discussed. The assignments are compared with those of related molecules to check the internal consistency and to obtain the pattern of the characteristic bands of thiocarbazoyl ($-CSNHNH_2$) group. The magnitudes of the C–N and S–CH_3 torsional barriers are estimated from the force constants.

The structural and spectroscopic studies[1–6] of the methyl ester of dithiocarbazic acid and its *N*-substituted derivatives are currently of interest. The impetus for this and similar work arises from the wide ranging applications of these compounds in industry and medicine[7,8] and their varying ligational[9] and conformational properties.[1,10] *S*-methyl dithiocarbazate (SMDTCZ) is itself a very interesting compound which has been isolated as solid in two planar molecular conformations[1,2] shown below (Fig. 1).

(a) *cis-trans* (b) *trans-cis*

Fig. 1.

The infrared spectra of SMDTCZ have been reported;[2,6] some assignments have been made empirically. In order to note more precisely the conformation-sensitive vibrations and discuss the vibrational spectra of SMDTCZ more fully, we have investigated the infrared spectra of SMDTCZ in two molecular conformations as well as their *N*-deuterated species. Based upon the force function previously developed,[11,12] normal coordinate analyses have been accomplished. The results are compared with those of chemically and structurally related molecules[11–15] for which detailed vibrational assignments have recently become available to provide a test for the general validity of the assignments derived and to obtain a pattern characteristic of the bands arising from thiocarbazoyl $-C(=S)NHNH_2$ grouping. The magnitude of the torsional barriers about the C–N and S–CH_3 bonds is estimated from the force constants.

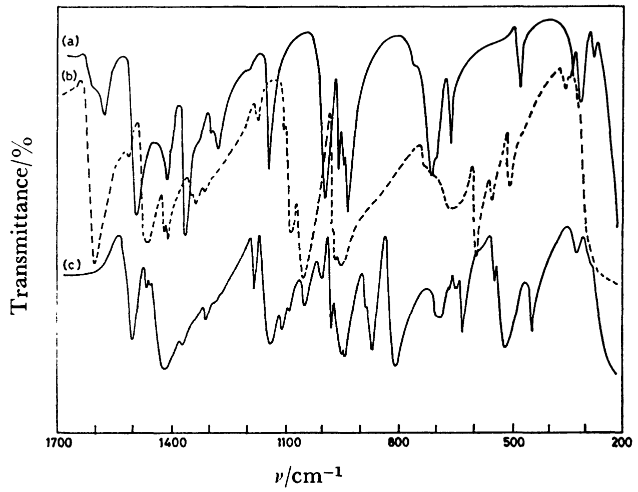

Fig. 2. Infrared spectra of SMDTCZ in (a) *cis-trans*, (b) *trans-cis*, and (c) of SMDTCZ-d_3 in *cis-trans* conformations.

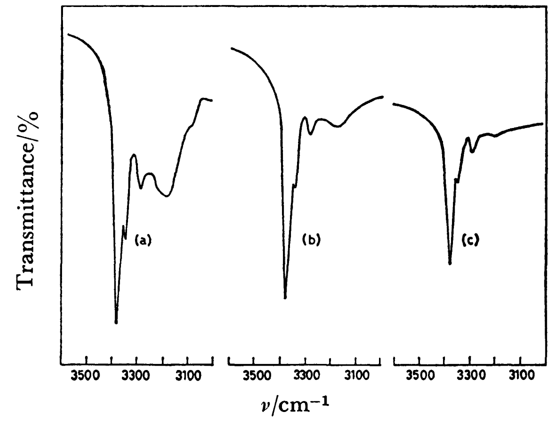

Fig. 3. Infrared spectra of *S*-methyl dithiocarbazate in $CHCl_3$ at concentrations of (a) 1.0×10^{-1} M, (b) 0.6×10^{-1} M, and 0.3×10^{-1} M ($1 M = 1 mol dm^{-3}$).

Experimental

SMDTCZ having *cis-trans* and *trans-cis* conformation was prepared according to the literature methods.[16,17] Recrystallization from aqueous solution of the *trans-cis* conformer yields the *cis-trans* conformer of SMDTCZ. The purity of the compounds was checked by microanalyses. The *N*-deuterated samples were obtained by repeated exchange reaction with D_2O.

The infrared spectra from 4000 to 200 cm^{-1} were measured on a Perkin-Elmer 580 spectrophotometer in KBr pellets and nujol mulls which yielded identical spectra. The observed spectra are shown in Fig. 2. The solution spectra were run on the same instrument using NaCl cells of path length of 0.4 mm (Figs. 3 and 4). The spectra between 400 and 30 cm^{-1} were recorded on a Polytec FIR 30 Michelson interferometer as polyethylene disks. The instruments were calibrated with usual standards.

Normal Coordinate Analysis

The conformations adopted for the calculations are shown in Fig. 1. In the molecular symmetry C_s, the 30 normal modes of vibration of SMDTCZ span

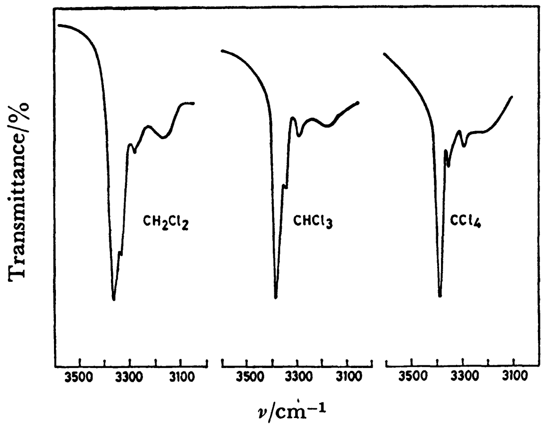

Fig. 4. Infrared spectra of *S*-methyl dithiocarbazate in different solvents.

19 of species a′ (in-plane) and 11 of species a″ (out-of-plane) vibrations. The internal and symmetry coordinates were selected in the usually accepted form. The bond length and valence angle values for SMDTCZ, were transferred from the X-ray crystal structure data.[1,2] The potential energy was expressed in terms of a Urey-Bradley force function employing valence force field type constants for the out-of-plane and torsional coordinates. The initial values of the force constants were transferred from thiosemicarbazide[11] (hydrazinecarbothioamide) and *S*-methyl *N*-methyldithiocarbamate.[12] The refinement of the force constants was carried out as already described.[11,12] The computations were made on a DEC 1090 digital computer employing a program similar in form to that of Schachtschneider.[18]

The final force constants of SMDTCZ listed in Table 1 are considered physically reasonable. Good fit reached between the observed and calculated frequencies for SMDTCZ and its deuterium labelled molecule also lends confidence to the values of the force constants and the assignments derived (Tables 2 and 3).

Results and Discussion

We noted that recrystallization of the *trans-cis* conformer of SMDTCZ from aqueous solution transformed it to the *cis-trans* form, while recrystallization from organic solvents including alcohols did not effect any conformational change, contrary to an earlier report.[2] Further, heating the *trans-cis* isomer to its melting and then cooling it also did not bring about any conformational change. The *N*-deuterated product of both isomeric forms of SMDTCZ interestingly yielded identical infrared spectrum; it was found to correspond to that of the *cis-trans* conformer which is the stablest form.

The frequencies of the observed infrared bands of SMDTCZ are listed in Table 2, together with the calculated vibrational frequencies along with approximate descriptions of the modes in terms of the potential energy distributions (PED) amongst the symmetry coordinates including only terms having greater than 15 percent for simplicity. Similar data for the *N*-deuterated compound are presented in Table 3. Despite the general asymmetry of the molecule, most of the fundamental frequencies may be described as group vibrations. A perusal of Table 2 shows that most of the frequencies for the two conformers differ, to a lesser or a greater extent.

N–H Stretching. The characteristic N–H stretching frequencies are sensitive to structural and electronic variations. The existence of conformational isomers in solution is clearly manifested in the infrared spectra of SMDTCZ (Figs. 3 and 4) which possess

Table 1. Force constants[a] of SMDTCZ in (a) *cis-trans* and (b) *trans-cis* conformations

(1) Urey-Bradley type constants								
	(a)	(b)		(a)	(b)		(a)	(b)
K(C=S)	3.80	4.05	H(NC=S)	0.46	0.40	F(NC=S)	1.15	1.15
K(C-S)	2.70	3.05	H(NC-S)	0.30	0.30	F(NC-S)	0.90	0.90
K(S-C)	2.10	1.90	H(SCS)	0.20	0.06	F(SCS)	0.40	0.45
K(CN)	6.15	5.45	H(CSC)	0.14	0.18	F(CSC)	0.15	0.15
K(NN)	3.60	4.20	H(CNN)	0.27	0.40	F(CNN)	0.35	0.35
K(N′H)	5.45	5.50	H(CNH)	0.27	0.27	F(CNH)	0.45	0.50
K(NH)	5.30	5.40	H(HNN)	0.12	0.08	F(HNN)	0.50	0.54
K(CH)	4.52	4.50	H(NNH)	0.09	0.06	F(NNH)	0.54	0.35
k(CH$_3$)	−0.08	−0.04	H(HNH)	0.60	0.64	F(HNH)	0.08	0.07
			H(SCH)	0.20	0.17	F(SCH)	0.40	0.40
			H(HCH)	0.40	0.36	F(HCH)	0.05	0.14
(2) Valence type constants								
	(a)	(b)		(a)	(b)			
f(πCS)	0.090	0.150	f(τCN)	0.085	0.060			
f(πNH)	0.044	0.060	f(τCS)	0.180	0.220			
f(tNH$_2$)	0.550	0.570	f(τCH$_3$)	0.008	0.007			
f(τNH$_2$)	0.030	0.024	f(πCS, τNH$_2$)	−0.012	0.014			

a) Units: K, H, F are in N cm^{-1} (=mdyn Å^{-1}) and k, f in 10^{-16} N cm rad^{-2} (=mdyn Å rad^{-2}); meaning of t, π, τ as in Table 3.

TABLE 2. OBSERVED AND CALCULATED FUNDAMENTALS (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION(PED) FOR SMDTCZ IN TWO CONFORMATIONS

			cis-trans			*trans-cis*
Species	Obsd	Calcd	Description[a)] (PED/%)	Obsd	Calcd	Description[a)] (PED/%)
a′	3280	3282	νNH(99)	3305	3311	νNH(100)
	3155	3157	νNH$_2$(99)	3175	3162	νNH$_2$(100)
	2960	2966	ν_aCH$_3$(100)	2975	2973	ν_aCH$_3$(100)
	2890	2886	ν_sCH$_3$(100)	2920	2947	ν_sCH$_3$(100)
	1598	1597	δNH$_2$(86)	1610	1608	δNH$_2$(92)
	1507	1502	νCN(54), δNH(27)	1465	1467	δNH(45), νCN(31)
	1420	1431	δ_aCH$_3$(82)	1412	1412	δ_aCH$_3$(88)
	1373	1385	δNH(47), νCN(25), νC=S(15)	1340	1344	νCN(54), δNH(25)
	1290	1288	δ_sCH$_3$(96)	1312	1309	δ_sCH$_3$(97)
	1155	1159	δNCS(28), νNN(20), νC=S(16)	1170	1183	δNCS(24), νC=S(21), νC–S(18)
	1005	1003	νNN(45), νC–S(30)	1080	1080	νNN(58), νC=S(30)
	955 945	950	rCH$_3$(73)	949	947	rCH$_3$(83)
	780	789	wNH$_2$(60)	727	724	νS–C(67), νC–S(17)
	725	728	νS–C(95)	655	662	wNH$_2$(30), νS–C(29), νC–S(23)
	705	693	νC=S(34), wNH$_2$(29)	582	585	wNH$_2$(63), νC–S(18)
	465	461	νC–S(45), δNCS(24)	496	499	δNNC(25), δNCS(24), νC=S(24)
	315	314	δSCS(62)	350	347	δSCS(50), δCSC(24)
	230	230	δNNC(60), δNCS(16)	222	222	δNNC(44), δNCS(31), δCSC(19)
	149	150	δCSC(71)	150	151	δCSC(53), δSCS(34)
a″	3180	3160	νNH$_2$(100)	3240	3246	νNH$_2$(100)
	2975	2966	νCH$_3$(100)	2975	2972	νCH$_3$(100)
	1430	1431	δCH$_3$(82), rCH$_3$(18)	1421	1412	δCH$_3$(88)
	1120	1119	tNH(100)	1047	1042	tNH$_2$(99)
	970	949	rCH$_3$(76), δCH$_3$(23)	964	945	rCH$_3$(84), δCH$_3$(15)
	665	666	τCN(47), τNH$_2$(32), πNH(21)	635	648	τCN(39), πNH(38), τNH$_2$(21)
	338	337	τNH$_2$(60), πNH(20)	290	297	πC=S(53), τNH$_2$(38)
	278	279	πC=S(53), τCN(22), τC–S(16)	260	270	τNH$_2$(41), πC=S(25), τCN(19)
	148	150	τC–S(62), πNH(17)	205	204	τC–S(73), τCN(18)
	135	133	τCH$_3$(42), πC=S(18), τC–S(16)	115	115	τCH$_3$(88)
	110	112	τCH$_3$(45), πC=S(22), πNH(21)	115	111	πNH(39), τCN(25), τC–S(18)

a) Meaning of ν, δ, r, t, w, π, τ as in Table 3.

two distinguishable bands in the N–H frequency region. The first band observed in the 3365—3390 cm^{-1} range is attributable to a *trans* –CS–NH– grouping and the second appearing in the 3340—3350 cm^{-1} interval to a *cis* –CS–NH– conformation. If we assume the extinction coefficients of the *cis* and *trans* forms to be nearly equal as is usually done, it is seen that the *cis-trans* conformer (a) with *trans* –NH–CS– grouping predominates in solution. Further, the relative intensities of the doublet peaks were found to be concentration independent (Fig. 3) ruling out the doublets being ascribed to molecular association. The infrared spectra of SMDTCZ in a series of solvents were obtained to note the influence of solvent dielectric on the spectra. The experimental data are presented in Fig. 4. It is observed that changing the solvent causes considerable alterations in the relative intensities of the two bands, which supports the presence of a conformational equilibrium. Increasing the solvent polarity favours transition to a *trans-cis* form (with *cis* –CS–NH– grouping). The spectra (Figs. 3 and 4) further exhibit a weak band around 3285 cm^{-1} and another weak but broad absorption centred around 3180 cm^{-1}. The former band has the characteristics of the intermolecularly hydrogen-bonded N–H stretching band; the region being same as in the solid. The latter absorption arise from the –NH$_2$ stretching motions.

According to the literature data, and as already pointed out, in the infrared spectra, of the two N–H stretching bands, a high frequency band is assigned to the *trans*(–NH–CS–) form and a low frequency band for the *cis* conformation. Interestingly, a reverse situation—the *trans* NH stretching band occurring at a lower frequency than the *cis* NH stretching mode—is realised for SMDTCZ in the solid phase. It may be ascribed essentially to intermolecular hydrogen bonding. Both rotamers exist as intermolecularly hydrogen bonded dimers. In the *cis-trans* isomer, N–H···N hydrogen bonds exist while in the *trans-cis* conformation N–H···S hydrogen bonds are present.[1,2] Since the former hydrogen bonds are stronger than the latter ones, the greater downward shift of the –NH stretching frequency may be expected pro-

TABLE 3. OBSERVED AND CALCULATED FUNDAMENTALS (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION (PED) FOR SMDTCZ-d_3

Species	Obsd	Calcd	Description$^{a)}$(PED/%)	Species	Obsd	Calcd	Description$^{a)}$(PED/%)
a′	2950	2966	$\nu_a CH_3$(100)		210	216	δNNC(59)
	2890	2886	$\nu_s CH_3$(100)		140	147	δCSC(67), δNCS(16)
	2420	2400	νND(98)	a″	2950	2966	νCH_3(100)
	2270	2284	νND_2(98)		2350	2335	νND_2(100)
	1490	1477	νCN(72)		1420	1431	δCH_3(82)
	1420	1431	$\delta_a CH_3$(82)		955	949	rCH_3(76), δCH_3(23)
	1286	1288	$\delta_s CH_3$(96)		815	836	tND_2(98)
	1240	1247	δNCS(26), νC=S(25), νNN(15)		520	484	τCN(46), τND_2(29), πND(24)
	1180	1175	δND_2(76)		310	295	πCS(40), τND_2(25), πND(16)
	982	992	νC-S(32), νNN(28)				
	955	948	rCH_3(69), $\delta_a CH_3$(21)		232	226	τND_2(47), τCN(28), πCS(17)
	945	936	δND(63), νNN(23)				
	712	728	νS-C(94)		—	149	τC-S(65), πND(15)
	700	719	νC=S(49)		133	130	τCH_3(57)
	625	588	wND_2(65)		105	108	τCH_3(30), πND(27), πCS(25)
	446	439	νC-S(38), δNCS(27)				
	305	311	δSCS(62)				

a) ν: Stretching, δ: deformation, r: rocking, t: twisting, w: wagging, π: out of plane bending, τ: torsion, a: asymmetric, s: symmetric.

TABLE 4. COMPARISON OF THE ASSIGNMENTS OF SMDTCZ WITH THOSE OF ITS RELATED MOLECULES

TSC	MMTU	TCH$^{a)}$	DMTU	MMDTC	SMDTCZ		Main assignments
					cis-trans	*trans-cis*	
3260 3180	3350 3139	3200	—	—	3180 3155	3240 3175	NH_2 stretching
3180	3230	3170	3305	3260	3280	3305	NH stretching
800	778	768	725	468	705	490	C=S stretching
1643	—	1620	—	—	1598	1610	NH_2 bend
1480	1302	1333	1355 1287	1349	1373	1465	NH bend+C-N stretching
1530	1500	1530^{t} 1488^{c}	1560 1506	1519	1507	1340	C-N stretching+NH bend
1160	1125	1140^{c} 1078^{t}	—	—	1005	1080	NN/CN stretching
995	—	1010^{c} 932^{t}	—	—	1120	1047	NH_2 twist
725	—	680^{c} 754^{t}	—	—	780	655	NH_2 wag
—	—	—	—	721	725	727	$S-CH_3$ stretching
570	—	579	662 642	556	665	635	N-H out-of-plane bend
408	496	468	445	356	465	496	C=S bend
353	—	307	445	440	278	290	C=S out-of-plane bend
—	—	—	—	174	149	150	CSC bend
206	—	253 194	—	—	230	228	NNC/CNC bend
				2930 2885	2960 2890	2975 2920	CH_3 stretching
				1409	1420	1412	CH_3 asymmetric bend
				1309	1290	1312	CH_3 symmetric bend
				946	955 945	949	CH_3 rock
				946	970	964	CH_3 wag
				106	110	115	CH_3 torsion

Abbrs. and (Refs.): TSC; thiosemicarbazide (11), NMTU; *N*-methylthiourea (15), TCH; thiocarbonohydrazide (13), DMTU; *N,N′*-dimethylthiourea (14), MMDTC; *N*-methyl *S*-methyldithiocarbamate (12), SMDTCZ; *S*-methyl dithiocarbazate (present work).

a) c and t refer to *cis* and *trans* groups to C=S bond.

ducing *cis*-NH band at a frequency higher than the *trans*-NH band.

Comparison. The assignments for SMDTCZ are compared with those available for related compounds[11-15] in Table 4. It is satisfactory that most of the assignments for SMDTCZ are compatible with the general features of the spectra of thiosemicarbazide and thiocarbonohydrazide and the pertinent portions from their isoelectronic thioureas and from *S*-methyl *N*-methyldithiocarbamate. Some of the differences in the characteristic frequencies could be explained on the basis of the different nature of the coupling with other vibrations. On the whole, there is internal consistency in the assignments and some pattern characteristic of –CSHN– grouping as well as those of the –HNNH$_2$ vibrations could be recognized. A brief discussion of the spectra of SMDTCZ will now be given.

–CSNHNH$_2$ Group Vibrations. An important band in the spectra of hydrazo derivatives is the N–N stretching band. The stretching frequency of N–N bond *cis* to C=S group is found 80 cm^{-1} lower than that for the *trans* N–N group. This is compatible with a similar assignment for *trans* and *cis* N–N bond stretching in thiosemicarbazide[11,21] but a reverse situation is found in thiocarbonohydrazide.[13] This may partly be explained on the basis of the mixing of the other vibrations.

The other bands of interest are those arising from the thioureide vibrations. The thioamide II and III bands arise from coupled modes of in-plane NH bending and C–N stretching; the former band is predominantly due to NH bending while the latter one arises chiefly from C–N stretching. These bands are conformation-sensitive. For SMDTCZ, the *trans* –CSNH– group has CN stretching band at a higher frequency than N–H in-plane bending. Similar findings have been made in other related systems.

The thioamide I band corresponding to C=S stretching is sensitive to the molecular environment and conformation. SMDTCZ provides a dramatic example of this; both rotamers have however no bands which could be attributed unequivocally to the C=S stretching mode.

The wagging and twisting modes of the –NNH$_2$ group appear to be conformation-sensitive. The vibrations of the –NH$_2$ group *cis* to the C=S moiety occur at higher wave numbers compared to –NH$_2$ group bands trans to the C=S grouping. A similar trend is noticeable for NH$_2$ torsional mode but is complicated by the more extensive mixing with other vibrations.

Torsional Barriers. From the value of the torsional force constants we may roughly estimate the potential barriers for C–N and S–C bonds. Following the procedures of Uno *et al.*,[22,23] we obtained 6.4 and 5.6 kJ mol^{-1} (1.53 and 1.34 kcal mol^{-1}) as barriers to internal rotation for S–CH$_3$ bond for the *cis-trans* and *trans-cis* conformers respectively. The values obtained are similar to that of acetamide[22] and *N*-methylurea[23] (5.4—7.1 kJ mol^{-1}). The C–N barrier is calculated to be 100.7 and 70.6 kJ mol^{-1} (24.06 and 16.87 kcal mol^{-1}) respectively for the *cis-trans* and *trans-cis* isomers, assuming an energy difference of 6.7 kJ mol^{-1} (1.6 kcal mol^{-1}) between the *cis* and *trans* NH$_2$ forms.[10] The estimates of the barrier heights over the amide C–N bond from torsional force constants in related thioamides and thioureas are similar and are usually higher than those determined by NMR methods.[24]

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