Vibrational spectra and force constants of *S*-methyl-*N*,*N*-dimethyldithiocarbamate

S. A. Katsyuba,★ L. V. Avvakumova, D. A. Pudovik, I. Kh. Shakirov, and R. R. Shagidullin

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan' Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: +7 (843 2) 752 253

The IR and Raman spectra of *S*-methyl-*N*,*N*-dimethyldithiocarbamate were studied in different phase states. The frequencies and vibration modes of normal vibrations were analyzed, and the erroneous assignments made in some previous works were corrected. The force constants of the molecule were estimated using the model of the generalized valence-force field.

Key words: *S*-methyl-*N*,*N*-dimethyldithiocarbamate, vibrational spectra, force constants.

The vibrational spectra of carbamates have been studied in detail, whereas their thioanalogs were described only in two reports[1,2] on the frequencies of the IR absorbtion bands of *S*-methyl-*N*,*N*-dimethyldithiocarbamate (**1**) and *S*-methyldithiocarbamate (**2**). The authors assigned these bands to the main vibrations of the molecules. A complete description of the IR spectra was not given in the works,[1,2] because the Raman spectra were not studied. The analysis of the frequencies and modes of the nonplanar normal vibrations of molecules **1** and **2** was carried out using the force constants of the generalized valence-force field, and the planar vibrations were analyzed using the Urey—Bradley model.[3] This complicates the use of the obtained force constants for the prediction and analysis of the spectra of related compounds.

Therefore a more detailed investigation of the vibrational spectra of dithiocarbamates is of interest. The results of such an investigation are given in the present work. We obtained the IR and Raman spectra of compound **1** in different phase states, performed a complete interpretation of the spectra, and estimated the force constants of molecule **1** within the frames of the united model of the generalized valence-force field.

Experimental

A sample of compound **1** was obtained by the reaction of dimethylamine with methyl iodide and carbon disulfide. The characteristic constants coincide with the literature data.[4] IR spectra were recorded on Specord 75IR and UR-20 spectrometers (400—4000 cm^{-1}), and Raman spectra were obtained on an RTI-30 spectrometer with an Ar$^+$ laser (λ = 4880 Å, spectral width of the slot 5 cm^{-1}, laser power 100 MW).

Polycrystalline samples for the registration of Raman spectra were sealed in glass capillaries filled with argon. To obtain the spectra of a melt, the capillary was heated using a device that maintained a constant temperature of the sample during recording of the spectrum. Liquid samples for IR spectra were prepared by melting the compound between KBr windows.

Crystal films were obtained by cooling the melt to the ambient temperature. The process of growing the crystals was monitored visually using crossed polaroids to get both disordered and well-oriented samples for polarization measurements.[5]

Results and Discussion

The parameters of the experimental spectra of the sample of **1** and their calculated interpretation are given in Table 1. We made a comparison with the data of other investigations[1] and changed the assignment of some vibrations of methyl groups. This revision was mainly caused by a comparison of the spectra of compound **1** with the recently published[6] ones of *S*-methyl-*N*,*N*-dimethylthiocarbamate (**3**). The interpretation of the latter seems to be fairly reliable, because it is based on the data on the vibrations of d$_3$-, d$_6$-, d$_9$-, and ^{13}C substituted isotopomers of **3** and on the results of the analysis of the frequencies and modes of normal vibrations.

In addition, unlike other authors,[1] we assigned to the off-planar vibrations of A'' symmetry the IR band at 964 cm^{-1} rather than the band at 950 cm^{-1}. The reason for this was the fact, that, according to our polarization measurement, the moment of the transition of the former vibration is perpendicular to the moments of the transitions at 994 and 976 cm^{-1}, which lie in the symmetry

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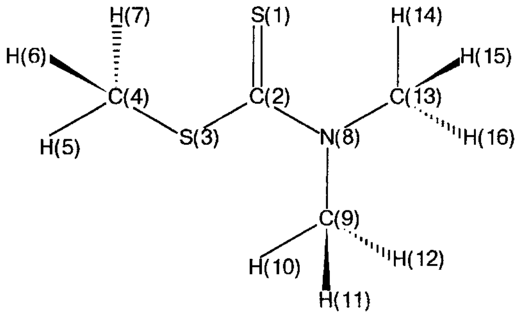
Table 1. Characteristics of the vibrational spectra of compound **1**

IR[a]		Raman		Calculation	
Crystal	Fusion	Crystal	Fusion	ν/cm^{-1} [b]	Assignment[c]
2995 w	2992 v.w	2995 m	2993 m	3000 (A')	ν_{as}((S)CH$_3$)
				2999 (A'')	ν_{as}((S)CH$_3$)
2950 v.w	2960 v.w			2958 (A'')	ν_{as}((N)CH$_3$)
				2958 (A'')	ν_{as}((N)CH$_3$)
2929 m	2930 sh			2933 (A')	ν_{as}((N)CH$_3$)
				2930 (A')	ν_{as}((N)CH$_3$)
2917 m	2919 s	2915 v.s	2915 v.s	2917 (A')	ν_s((S)SH$_3$)
2872 v.w	2880 v.w	2860 w			
	2838 v.w				
	2800 v.w	2800 v.w		2798 (A')	ν_s((N)CH$_3$)
				2797 (A')	ν_s((N)CH$_3$)
1520 m	1500 v.s	1505 v.w		1513 (A')	ρS(2)N, ρNC(2), δ_s((N)CH$_3$), ν_{as}NC(2), ν(C=S)
1452 m		1447 w		1447 (A'')	δ_{as}((N)CH$_3$)
				1446 (A'')	δ_{as}((N)CH$_3$)
			1440 br	1441 (A')	δ_{as}((N)CH$_3$)
1428 m	1425 w			1433 (A')	δ_{as}((N)CH$_3$)
1410 m	1408 m	1405 w	1405 w	1410 (A'')	δ_{as}((S)CH$_3$)
				1402 (A')	δ_{as}((S)CH$_3$)
1396 w			1395 w	1400 (A')	δ_s((N)CH$_3$), δ_{as}((S)CH$_3$), ν(C(2)N)
	1377 v.s	1374 m	1370 w	1370 (A')	δ_s((S)SH$_3$), ν_{as}(C(2)NC(9))
		1335 v.w	1338 v.w		
1320 w	1320 w	1310 v.w		1315 (A')	δ_s((S)CH$_3$)
1257 v.s	1257 v.s	1247 w	1250 v.w	1248 (A')	ν(C(2)N), ν(C(2)S), δ((N)CH$_3$), δNC$_2$
		1145 v.w	1148 w		
1145 v.w	1136 s	1130 v.w	1125 w	1135 (A'')	ρ((N)CH$_3$)
				1060 (A')	ρ((N)CH$_3$), ν(C=S), ν(C(2)S), ν_{as}(NC$_2$)
1050 w	1048 m				
				1047 (A'')	ρ((N)CH$_3$)
994 v.s	995 v.s		1000 w	1000 (A')	ρ((N)CH$_3$), ν(C(2)N), ν(S(2)S)
976 v.s	980 m	980 v.w	980 v.w	972 (A')	ρ((S)CH$_3$), ν(C(2)S), ν_{as}(NC$_2$)
964 v.s	953 s		960 w	954 (A'')	ρ((S)CH$_3$)
950 v.s			953 v.w	945 (A')	ρ((S)CH$_3$), ν_{as}(NC$_2$), ν(C=S), ν(C(2)S)
872 v.w	870 m				
839 v.w	839 v.w			843 (A')	ν_s(NC$_2$), ρ((N)CH$_3$)
730 w	728 v.w	729 m	727 m	735 (A')	ν(SC(2))
575 w	573 m	572 v.s	569 s	570 (A')	δ(NC$_2$), δ(CS$_2$), ν_s(NC$_2$), ν_s(CS$_2$)
563 v.w					
447 w	447 m	447 m	445 w	451 (A')	ν(C=S), ν_{as}(NC$_2$), ρ(NC$_2$)
424 w	419 m	417 m	418 m	424 (A')	ν_s(CS$_2$), ρ(NC$_2$), δ(CSC)
390		378 v.w	382 m	393 (A'')	ρ(C=S), χ(C(2)S), χ_{as}((N)CH$_3$), ω(NC$_2$)
		345 m	340 w		
300				313 (A')	δ(CSC), δ(CS$_2$), δ(NC$_2$)
240				246 (A'')	w(NC$_2$), χ_{as}((N)CH$_3$)
220				212 (A')	ρ(C=S)
184				179 (A'')	χ_s((N)CH$_3$), τ(NC$_2$)
175				170 (A')	δ(S—C—N)

Table 1. (Continued)

IR[a]		Raman		Calculation	
Crystal	Fusion	Crystal	Fusion	ν/cm^{-1} [b]	Assignment[c]
152				150 (A'')	$\chi_s((N)CH_3)$
121				119 (A'')	$\chi_{as}((N)CH_3)$, $w(NC_2)$, $\chi((S)CH_3)$
115				117 (A'')	$\chi((S)CH_3)$
			110 w		
99		100 v.s		99 (A'')	$\rho(C{=}S)$, $\chi_{as}((N)CH_3)$, $\chi(C(2)S)$

[a] Frequencies of the IR bands lower than 400 cm^{-1} are taken from Ref. 1. [b] In brackets the symmetry of the vibration is given. [c] Type of vibration: ν — stretching, δ — deformational, ρ — rocking, τ — twisting, χ — torsion, w — fan, s — symmetrical, as — asymmetrical.



1

plane of the molecule (A' symmetry of vibrations), whereas the moment of the vibration at 950 cm^{-1} is parallel to the same moments.

The frequencies and modes of the normal vibrations of compound **1** were initially calculated on the basis of a potential field obtained by transfer of the force constants of the molecule of **3** (cf. Ref. 6). Comparison of the spectra of the molecule of **1** in various states of aggregation confirmed the literature data[1] about only one conformation being possible for this molecule (the geometric parameters of the molecule of **1** were taken from Ref. 1).

The following torsion angles (χ) were used as the torsion coordinates: χ_1 (between the planes of the atoms S(1), C(2), S(3) and C(9), N(8), C(13), respectively) for the description of the vibrations around the C(2)—N(8) bond; χ_2 = S(1)—C(2)—S(3)—C(4), around the C(2)—S(3) bond; χ_3 = C(2)—S(3)—C(4)—H(5), around the S(3)—C(4) bond; χ_4 = C(2)—S(8)—C(9)—H(10), around the N(8)—C(9) bond; χ_5 = C(2)—N(8)—C(13)—H(14), around the N(8)—C(13) bond. The spectral mass was used for hydrogen atoms (1.088 amu).[3] The initial values of the force constants were varied to make the deviations between the calculated and experimental frequencies not exceed the standard experimental errors. The force field derivatives of the frequencies were used in calculations.[3]

The following values of the parameters of the potential field of molecule **1** were obtained as a result of the variation: $K_{\mathrm{S(1)C(2)}} = 5.50$, $K_{\mathrm{NC(2)}} = 10.20$, $K_{\mathrm{NC(9)}} = 6.53$, $K_{\mathrm{S(3)C(2)}} = 5.89$, $K_{\mathrm{S(3)C(4)}} = 5.38$, $K_{\mathrm{C(4)H}} = 8.075$, $K_{\mathrm{C(13)H(14)}} = K_{\mathrm{C(9)C(10)}} = 7.57$, $K_{\mathrm{C(9)H(11)}} = K_{\mathrm{C(9)H(12)}} = K_{\mathrm{C(13)H(15)}} = K_{\mathrm{C(13)H(16)}} = 7.69$, $K_{\mathrm{NC(2)S(1)}} = 2.97$, $K_{\mathrm{C(2)S(3)C(4)}} = K_{\mathrm{C(2)NC(13)}} = 1.99$, $K_{\mathrm{S(3)C(4)H}} = 0.85$, $K_{\mathrm{NCH}} = 1.00$, $K_{\mathrm{HC(4)H}} = 0.684$, $K_{\mathrm{HC(13)H}} = K_{\mathrm{HC(9)H}} = 0.71$, $K_{\mathrm{S(1)C(2)N}} = K_{\mathrm{S(1)C(2)S(3)}} = 1.32$, $K_{\mathrm{C(2)NC(9)}} = K_{\mathrm{C(2)NC(13)}} = 1.85$, $\rho^{\mathrm{S(3)C(2)N}}_{\mathrm{S(1)C(2)}} = 0.24$, $\rho^{\mathrm{C(9)NC(13)}}_{\mathrm{NC(2)}} = 0.156$, $\chi^{\mathrm{C(9)NC(13)}}_{\mathrm{S(1)C(2)S(3)}} = 1.099$, $\chi^{\mathrm{C(2)S(3)C(4)}}_{\mathrm{S(1)C(2)S(3)}} = 0.47$, $\chi^{\mathrm{S(3)C(4)H(5)}}_{\mathrm{C(2)S(3)C(4)}} = 0.037$, $\chi^{\mathrm{NC(9)H(10)}}_{\mathrm{C(2)NC(9)}} = 0.054$, $H^{\mathrm{C(2)S(1)}}_{\mathrm{NC(2)}} = 1.814$, $H^{\mathrm{C(2)S(3)}}_{\mathrm{C(2)S(1)}} = -0.550$, $H^{\mathrm{C(2)S(3)}}_{\mathrm{C(2)N}} = 1.82$, $H^{\mathrm{C(2)N}}_{\mathrm{C(9)N}} = H^{\mathrm{C(2)N}}_{\mathrm{C(13)N}} = 1.799$, $H^{\mathrm{S(3)C(4)}}_{\mathrm{C(2)S(3)}} = 0.16$, $H^{\mathrm{C(4)H}}_{\mathrm{C(4)H}} = 0.085$, $H^{\mathrm{C(9)H(11)}}_{\mathrm{C(9)H(10)}} = H^{\mathrm{C(9)H(12)}}_{\mathrm{C(9)H(10)}} = H^{\mathrm{C(13)H(15)}}_{\mathrm{C(13)H(14)}} = H^{\mathrm{C(13)H(16)}}_{\mathrm{C(13)H(14)}} = -0.020$, $H^{\mathrm{C(9)H(12)}}_{\mathrm{C(9)H(11)}} = H^{\mathrm{C(13)H(16)}}_{\mathrm{C(13)H(15)}} = -0.073$, $H^{\mathrm{NC(13)}}_{\mathrm{NC(9)}} = 0.803$, $A^{\mathrm{NC(2)S(3)}}_{\mathrm{C(2)S(1)}} = -0.800$, $A^{\mathrm{S(1)C(2)S(3)}}_{\mathrm{C(2)S(1)}} = A^{\mathrm{S(1)C(2)N}}_{\mathrm{C(2)S(1)}} = 0.8$, $A^{\mathrm{NC(2)S(3)}}_{\mathrm{NC(2)}} = -0.325$, $A^{\mathrm{S(3)C(2)S(1)}}_{\mathrm{NC(2)}} = 0.715$, $A^{\mathrm{NC(2)S(1)}}_{\mathrm{NC(2)}} = 1.999$, $A^{\mathrm{C(2)NC(13)}}_{\mathrm{NC(2)}} = A^{\mathrm{C(2)NC(9)}}_{\mathrm{NC(2)}} = -0.086$, $A^{\mathrm{S(1)C(2)S(3)}}_{\mathrm{C(2)S(3)}} = A^{\mathrm{S(3)C(2)N}}_{\mathrm{C(2)S(3)}} = 0.275$, $A^{\mathrm{C(4)S(3)C(2)}}_{\mathrm{C(2)S(3)}} = 0.279$, $A^{\mathrm{C(2)S(3)C(4)}}_{\mathrm{S(3)C(4)}} = 0.429$, $A^{\mathrm{S(3)C(4)H}}_{\mathrm{S(3)C(4)}} = 0.629$, $A^{\mathrm{C(2)NC(9)}}_{\mathrm{C(9)N}} = A^{\mathrm{C(2)NC(13)}}_{\mathrm{C(13)N}} = -0.20$, $A^{\mathrm{C(9)NC(13)}}_{\mathrm{C(9)N}} = A^{\mathrm{C(9)NC(13)}}_{\mathrm{C(13)N}} = 0.243$, $A^{\mathrm{NC(9)H}}_{\mathrm{NC(9)}} = A^{\mathrm{NC(13)H}}_{\mathrm{NC(13)}} = 0.715$, $l^{\mathrm{S(3)C(2)N}}_{\mathrm{S(1)C(2)S(3)}} = 0.6$, $l^{\mathrm{S(3)C(2)N}}_{\mathrm{S(1)C(2)N}} = 0.4$, $l^{\mathrm{NC(13)H}}_{\mathrm{C(9)NC(13)}} = l^{\mathrm{NC(9)H}}_{\mathrm{C(9)NC(13)}} = 0.2$, ${}^{\mathrm{S(3)C(2)N}}_{\mathrm{S(1)C(2)}}\phi^{\mathrm{C(9)NC(13)}}_{\mathrm{C(9)NC(2)}} = 0.05$, ${}^{\mathrm{S(3)C(2)N}}_{\mathrm{S(1)C(2)}}\phi^{\mathrm{C(2)S(3)C(4)}}_{\mathrm{S(1)C(2)S(3)}} = 0.075$, ${}^{\mathrm{NC(9)H(9)}}_{\mathrm{C(2)NC(9)}}\phi^{\mathrm{NC(13)H(14)}}_{\mathrm{C(2)NC(13)}} = 0.008$ (the dimension of the parameters is $10^6\ \mathrm{cm}^{-2}$, designations are similar to those reported previously.)[3]

The interpretation of the spectra made with the use of these parameters is given in Table 1.

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References

1. K. R. Gayathry Devi and D. N. Sathyanarayana, *Indian J. Chem.*, 1980, **19A**, 1082.

2. K. R. Gayathry Devi, D. N. Sathyanarayana, and S. Monogaran, *Spectrochim. Acta*, 1981, **37A**, 31.
3. G. S. Koptev and Yu. A. Pentin, *Raschet kolebanii molekul* [*Calculations of Molecule Vibrations*], Moscow Univers. Press, Moscow, 1977, p. 212.
4. C. H. Yoder, A. Komiya, J. E. Kochanowski, and F. H. Suydam, *J. Am. Chem. Soc.*, 1971, **93**, 6515.
5. A. I. Fishman, A. A. Stolov, and A. B. Remizov, *Spectrochim. Acta*, 1993, **49A**, 1435.
6. G. Keresztury, G. Besenyei, and S. Holly, *J. Mol. Structure*, 1990, **218**, 237.

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