Vibrational Spectra and Crystal and Molecular Structure of *trans,cis*-*S*-Methyl Dithiocarbazate, a Second Conformer

By **Rainer Mattes** * and **Harald Weber**, Anorganisch-chemisches Institut der Universität Münster, Gievenbecker Weg 9, 4400 Münster, Federal Republic of Germany

A second conformer (*trans,cis*) of *S*-methyl dithiocarbazate has been obtained by crystallisation at low temperature. It is triclinic with unit-cell dimensions a = 4.181(2), b = 6.067(2), c = 11.395(4) Å, α = 90.90(3), β = 111.19(3), γ = 92.85(3)°, and Z = 2. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to R 0.067 using 701 reflections. The structure comprises centrosymmetric dimers linked by N–H · · · S hydrogen bonds, in contrast to the *cis,trans* conformer where N–H · · · N bonds are present. The vibrational spectra of both conformers differ markedly, but the change of conformation does not significantly alter the bond distances and angles.

THERE has been much interest in *S*-methyl dithiocarbazate and its behaviour as a ligand towards transition metals.[1-3] A recent X-ray diffraction study on this compound has shown that the *cis,trans*-conformer is present in the solid state.[4] According to n.m.r. spectra,[5] supported by theoretical studies,[6] two or three conformers (*cis,cis*; *cis,trans*; and *trans,cis*) are present in solution. By crystallisation from ethanol–water (2 : 3) below 0 °C we have obtained a second conformer in the solid state. We report i.r. and Raman spectral and X-ray diffraction studies on this conformer of *S*-methyl dithiocarbazate.

EXPERIMENTAL

The ester was prepared as in refs. 7 and 8 at 0—10 °C. Needle-like crystals, m.p. 80.7 °C, were obtained from the mother liquor at −20 °C. Recrystallisation from benzene, chloroform, *etc.* leads invariably to the known *cis,trans* conformer. Transformation was also observed in the solid state above 30 °C, probably *via* the vapour phase.

Infrared and Raman spectra were measured with Perkin-Elmer 457 and Coderg T 800 spectrometers, respectively.

Crystal Data.—$C_2H_6N_2S_2$, M = 122.20, Triclinic, a = 4.181(2), b = 6.067(2), c = 11.395(4) Å, α = 90.90(3), β = 111.19(3), γ = 92.85(3)°, U = 269.0 Å^3, D_m = 1.52 g cm^{-3} (by flotation), Z = 2, D_c = 1.51, $F(000)$ = 128, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 8.1 cm^{-1}, space group $P\bar{1}$.

Structure Determination.—The crystal, selected for data collection on a Syntex $P2_1$ diffractometer at −120 °C, had dimensions *ca.* 0.40 × 0.25 × 0.15 mm. 1 191 Independent reflections with $2\theta < 54°$ were measured by use of the θ—2θ scan technique with variable scan speed (2.5—29.3° min^{-1}). 1 088 Reflections had $I > 1.96\sigma(I)$ but due to imperfections of the crystal 387 reflections monitored by the data-reduction program TAPER were imperfectly centred or had ' background imbalance.' Therefore, after correction for Lorentz and polarisation effects, only 701 reflections were used in the structure analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using anisotropic thermal parameters. All hydrogen atoms were located directly from difference syntheses. Their positional parameters were then included in the refinement. The weighting scheme used was $w = [\sigma^2(F_o) + (0.2F_o)^2]^{-1}$. Refinement converged at R = 0.067, R' = 0.095.

Structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22687 (5 pp.).† All calculations were performed on a Nova computer with the Syntex E-XTL program system.

RESULTS AND DISCUSSION

Tiripicchio and his co-workers[4] have recently described the solid-state structure of the *cis,trans* conformer of *S*-methyl dithiocarbazate. We have now found a second crystalline modification which contains the molecule in the *trans,cis* conformation. This conformation has already been postulated to exist in solution. The structural parameters are in Tables 1 and 2.

TABLE 1

Fractional atomic co-ordinates for *S*-methyl dithiocarbazate (non-hydrogen × 10^4, hydrogen × 10^3), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
S(1)	6 981(3)	4 545(2)	3 553(1)
S(2)	1 624(3)	2 269(2)	1 216(1)
N(1)	4 784(11)	6 152(6)	1 339(3)
N(2)	7 167(12)	7 889(7)	1 938(4)
C(1)	4 380(12)	4 398(7)	1 959(3)
C(2)	5 767(17)	1 994(9)	4 115(4)
H(1)	582(18)	51(11)	374(6)
H(2)	344(20)	192(11)	389(6)
H(3)	681(16)	219(10)	510(5)
H(4)	350(17)	632(11)	53(6)
H(5)	872(19)	794(11)	143(6)
H(6)	708(18)	957(11)	180(6)

The structure comprises centrosymmetric dimers linked by means of N–H · · · S hydrogen bonds, involving the imino-nitrogen and thiono-sulphur atoms (Figure 1). The hydrogen atom of the N–H group points in the direction of one lone pair of the sulphur atom. The dimers are linked to sheets in the (001) plane by bifurcated hydrogen bonds originating in the amino-group and pointing again to the thiono-sulphur atoms of two different molecules superimposed along the a axes. The *N,N*-dimethyl derivative of the *S*-methyl dithiocarbazate forms similar N · · · S hydrogen-bridged dimers.[4] This structural feature forces the hydrazido-group into *trans* conformation and allows the S-ester group the usual[9] *cis* conformation. In the closely related *S*-methyl monothiocarbazate the S-ester group also has a *cis* conformation.[10]

The differences in the conformation of the ester are not accompanied by significant differences in bond distances. Only the angles S(1)–C(1)–S(2) and N(1)–C(1)–S(1) differ significantly in the *trans,cis* and *cis,trans* conformers [125.5(3) and 113.6(3)° *vs.* 116.2(1) and

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

119.3(1)°], respectively. This is a consequence of the participation of S(2) in the hydrogen bonds in the *trans,cis* conformer, and of the change in conformation of the S-ester group.

The N ··· S distance of the ' short ' hydrogen bridge is significantly shorter than the same distance in *S*-methyl *N,N*-dimethyldithiocarbazate [3.358(5) *vs.* 3.480(4) Å] and is comparable to the distances found in dimethylammonium dimethyldithiocarbamate [11] and di-isopropylammonium di-isopropyldithiocarbamate.[12] This trend is also valid for the bifurcated bridge.

TABLE 2

Bond distances and angles in *trans,cis*-*S*-methyl dithiocarbazate

(*a*) Distances (Å)			
C(1)–S(1)	1.745(4)	C(2)–H(1)	1.00(7)
C(1)–S(2)	1.681(5)	C(2)–H(2)	0.91(8)
C(2)–S(1)	1.803(6)	C(2)–H(3)	1.05(6)
N(1)–C(1)	1.324(6)	N(1)–H(4)	0.90(8)
N(1)–N(2)	1.396(6)	N(2)–H(5)	1.01(8)
		N(2)–H(6)	1.03(7)
(*b*) Angles (°)			
C(1)–S(1)–C(2)	102.6(2)	H(6)–N(2)–N(1)	130(4)
S(1)–C(1)–S(2)	125.5(3)	H(6)–N(1)–H(5)	84(6)
S(1)–C(1)–N(1)	113.6(3)	H(1)–C(2)–H(2)	94(6)
S(2)–C(1)–N(1)	120.9(4)	H(1)–C(2)–H(3)	117(5)
C(1)–N(1)–N(2)	121.2(4)	H(2)–C(2)–H(3)	106(5)
H(4)–N(1)–N(2)	117(4)	H(1)–C(2)–S(1)	124(4)
H(4)–N(1)–C(1)	122(4)	H(2)–C(2)–S(1)	108(5)
H(5)–N(2)–N(1)	103(4)	H(3)–C(2)–S(1)	105(4)
(*c*) Hydrogen bonds and short intermolecular contacts			
S(2) ··· N(1^{I})	3.358(5)	S(2) ··· H(6^{III})	2.72(7)
S(2) ··· H(4^{I})	2.54(7)	S(2^{I}) ··· H(4)–N(1)	153(11)
S(2) ··· N(2^{II})	3.524(6)	S(2^{II}) ··· H(6)–N(2)	130(9)
S(2) ··· H(6^{I})	2.76(7)	S(2^{III}) ··· H(6)–N(2)	128(10)
S(2) ··· N(2^{III})	3.449(6)	H(4) ··· S(2)–C(1)	110(3)

Roman numeral superscripts denote the following equivalent positions: I $-x, 1-y, -z$; II $x, y-1, z$; III $x-1, y-1, z$.

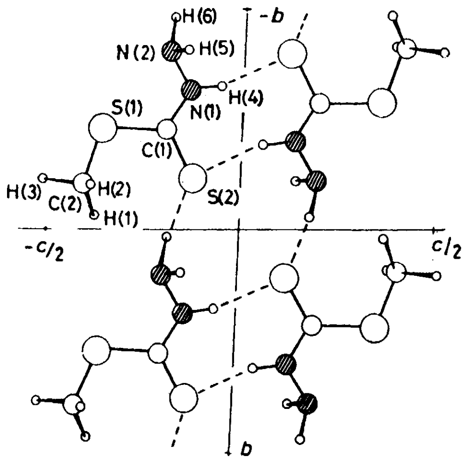

FIGURE 1 Molecular structure and atom-numbering scheme for *S*-methyl dithiocarbazate. Hydrogen bonds are shown as broken lines

The solid-state vibrational spectra of the two conformers now known differ markedly (see Figure 2) despite the close similarity in bond distances. This means that the spectral properties are influenced chiefly by the geometrical differences. All vibrational modes must therefore be highly coupled. The spectra of the *cis,trans* conformer and the closely related compounds $[Ni(NH_2NCSSCH_3)_2]$,[13] $[Ni(NH_2NHCSS)_2]$,[14] and $K[NH_2NHCSS]$ [15] have already been studied using isotopic substitution and normal-co-ordinate analyses.

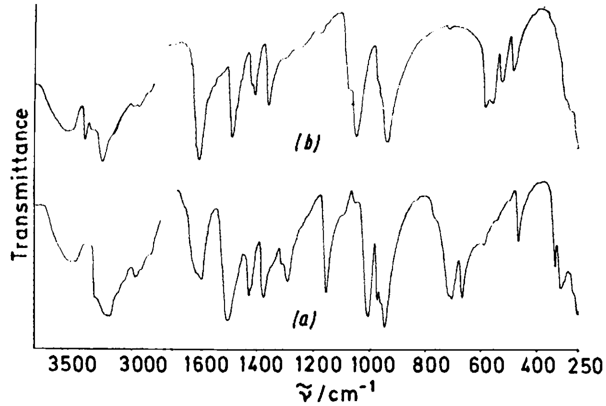

FIGURE 2 Infrared spectra of (*a*) *cis,trans*- and (*b*) *trans,cis*-*S*-methyl dithiocarbazate

Our band assignments are shown in Table 3. The following pronounced differences in the spectra of the two conformers exist. The NH and NH_2 stretching modes of the *cis,trans* conformer are observed at lower wavenumbers due to the presence of strong NH ··· N hydrogen bonds. The strong band at 1 155 cm^{-1} with a high contribution from the C=S stretching mode is absent in the *trans,cis* conformer. In this conformer the sulphur atom is involved in rather strong hydrogen bonds. The band with the highest intensity in the Raman spectra of both conformers has to be assigned to the breathing mode at the central carbon atom, with predominantly ν(C–S) character. This mode is shifted to lower wavenumbers by *ca.* 80 cm^{-1} in the spectrum of the *trans,cis* compared to the *cis,trans* conformer, probably due to the NH ··· S bonds and the opposite

TABLE 3

Vibrational bands (cm^{-1}) and assignments for *cis,trans*- and *trans,cis*-*S*-methyl dithiocarbazate (bands from the Raman spectra are marked with an asterisk)

cis,trans	*trans,cis*	Assignment
3 270w *	3 302m *	ν(NH)
3 225w *	3 260m *	$\nu_{asym}(NH_2)$
3 155m *	3 195s *	$\nu_{sym}(NH_2)$
1 600m,br	1 610vs	$\delta(NH_2)$
1 505s	1 490s	δ(NH)
1 428m	1 410m	$\delta_{asym}(CH_3)$
1 373m	1 365m	ν(CN)
1 312w (sh)	1 300vw	$\delta_{sym}(CH_3)$
1 290m	1 175vw	$\rho_w(NH_2)$
1 155s	1 078m (sh)	ν(C=S)
1 005vs	1 048vs,br	$\rho_\tau(NH_2)$
970s	978m (sh)	ν(NN)
945vs,br	940vs,br	$\rho(CH_3)$
705s	720vw	$\nu(S{-}CH_3)$
665s (678vs *)	589s (595vs *)	ν(C–S)
572m (sh)	560m	γ(NH)
	530m	$\gamma(NCS_2)$
465m (473s *)	490m (500vs *)	δ(NNC)

conformation of the S-ester group in the former conformer. However, without a normal-co-ordinate analysis these differences cannot be completely explained.

In a Raman spectrum of a solution of *S*-methyl dithiocarbazate in ethanol the most intense bands of both conformers can be observed. This indicates the presence of approximately equal amounts of the *cis,trans* and *trans,cis* conformers in solution, in accordance with the n.m.r. measurements.[5]

S-Methyl dithiocarbazate is the first hydrazine derivative for which different conformers have been found in the solid state, in solution, and in transition-metal complexes.[16] Only one conformer has been found so far for the related compounds *S*-methyl monothiocarbazate (*trans,cis*), *O*-methyl monothiocarbazate (*trans,cis*), and the monothiocarbazate ion (*cis* conformation with respect to the oxygen atom).[10]

[9/672 *Received*, 30*th April*, 1979]

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