Derivatives of Hydrazine. XII. Rotational Isomerism of Methyl Dithiocarbamates and Dithiocarbazates

BRITTA MYNSTER DAHL and PER HALFDAN NIELSEN

Department of General and Organic Chemistry, University of Copenhagen, The H. C Ørsted Institute, DK-2100 Copenhagen, Denmark

The ^{1}H NMR spectra have been recorded for a series of methyl dithiocarbamates and dithio-carbazates carrying one or more N-alkyl substituents. Signals attributed to the occurrence of Z and E isomers have been observed. The multiplicity, position, and solvent shifts at -20 °C are tabulated. The assignment of the Z and E isomers is based upon comparison of the spectral data with those of two cyclic dithio-carbazates which are necessarily Z isomers. The assignment is in harmony with results obtained for methyl diselenocarbamates and diseleno-carbazates and furthermore support Bauman's interpretation of the ^{1}H NMR spectra of thiono-carbamate esters.

A study of the variable temperature ^{1}H NMR spectra in a series of Se-methyl N^2-methyl-diselenocarbazates and -carbamates [1] has demonstrated the occurrence of hindered rotation around the N^2-C bond (Fig. 1, $Y=Se$). Based on these results three deductions were possible. (1) The N^2-CH_3 group cis to the $C=Y$ group always gives rise to a signal at lower field than the same group $trans$ to the $C=Y$ group. (2) In nitrobenzene solution, the low-field N^2-methyl resonance is shifted downfield relative to $CDCl_3$ solution while the high-field N-methyl resonance

is shifted upfield. (3) In CCl_4 solution, the signal from the N^2-CH_3 group in the Z isomer is displaced towards higher field relative to the position in $CDCl_3$ solution, while the signal from the N^2-CH_3 group in the E isomer is almost unaffected by this change in solvent.

The generalisations (1) and (3) have been found to be valid for the corresponding sulfur compounds. In order to obtain well-resolved signals from the Z and E isomers it was necessary to work below the m.p. of nitrobenzene (6 °C) and accordingly the validity of the generalisation (2) could not be tested. Holloway and Gitlitz [2] showed that hindered rotation of di-thiocarbamate esters leads to the appearance of signals assigned to E and Z forms by low temperature ^{1}H NMR spectroscopy. This has also been demonstrated in the case of N,N-diisopropyldithiocarbazic esters [3] and O-phenyl N,N-diisopropylthiocarbazate,[4] but in the two last cases the occurrence of additional dipolar forms represented an extra complication. Since these can only occur in carbazates containing the unsubstituted N^2-H group, we chose for the present study the dithiocarbazates $1-3$ (Fig. 1, $Y=S$). The well-known isomerism [2,5] of methyl dimethyldithiocarbamate (4) was rein-vestigated. Methyl N-ethyl-N-methyldithiocar-bamate (5) and methyl N-isopropyl-N-methyl-dithiocarbamate (6) were included for steric comparison with 2 and 3.

When the ^{1}H NMR spectra of $1-6$ were recorded at $ca.$ 40 °C each type of protons exhibits only one signal (singlet or multiplet). This reflects the state of rapid interconversion on the NMR time scale between the possible
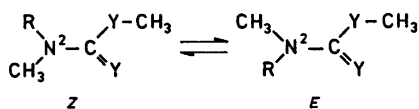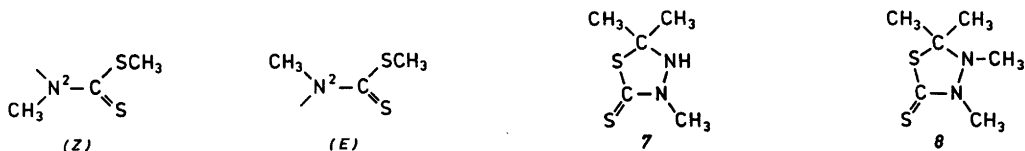

Fig. 1.

Compound	R	Compound	R
1	NH₂	4	CH₃
2	NHCH₃	5	CH₃CH₂
3	N(CH₃)₂	6	(CH₃)₂CH

Table 1. ¹H NMR chemical shifts (δ) of 3 % solutions of *N*-alkyl substituted methyl dithiocarbazates and dithiocarbamates at −20 °C and 1,3,4-thiadiazolidine-2-thiones at 40 °C in CCl_4, $CDCl_3$, CD_3NO_2, and C_6D_5Br.

Signal from	Solvent	Compound 1^d	2	3	4	5^f	6^g	7	8
%Z^h	$CDCl_3$	50	80	100	(50)	45	45	(100)	(100)
	CD_3NO_2	86	94	100	(50)	45	40	(100)	(100)
	CCl_4		75	100	(50)	45	40	(100)	(100)
	C_6D_5Br	50	75	100	(50)	47	41	(100)	(100)
N²-CH₃ (Z)	$CDCl_3$	3.81s	3.68s	3.43s	3.63s	3.54s	3.38s	3.51s	3.51s
	CD_3NO_2	3.71s	3.62s	3.41s	3.54s	3.49s	3.36s	3.45s	3.47s
	CCl_4		3.60s	3.37s	3.56s	3.46s	3.31s	3.43s	3.44s
	C_6D_5Br	3.23s	3.33s	3.13s	3.17s	3.22s	3.13s	3.25s	3.25s
N³-CH₃ (Z)	$CDCl_3$		2.73d^a	2.62s					2.72s
	CD_3NO_2		2.69^b	2.64s					2.70s
	CCl_4		2.73d	2.65s					2.66s
	C_6D_5Br		2.27d	2.14s					2.24s
S-CH₃ (Z)	$CDCl_3$	2.55s	2.48s^c	2.48s		2.67s^e	2.67s		
	CD_3NO_2	2.40s	2.39s^c	2.39s		2.57s^e	2.59s		
	CCl_4		2.39s^c	2.37s		2.52s^e	2.55s		
	C_6D_5Br	2.43s	2.45s^c	2.47s		2.58s^e	2.53s		
N²-CH₃ (E)	$CDCl_3$	3.58s	3.48s		3.44s	3.37s	3.19s		
	CD_3NO_2	3.57s	3.48s		3.42s	3.38s	3.21s		
	CCl_4		3.47s		3.44s	3.34s	3.17s		
	C_6D_5Br	3.00s	3.08s		2.80s	2.92s	2.80s		
N³-CH₃ (E)	$CDCl_3$		2.70d						
	CD_3NO_2		2.65^b						
	CCl_4		2.67d						
	C_6D_5Br		2.40d^a						
S-CH₃ (E)	$CDCl_3$	2.69s	2.68s^c		2.67s^e	2.67s	2.68s		
	CD_3NO_2	2.61s	2.65s^c		2.57s^e	2.59s	2.60s		
	CCl_4		2.63s^c		2.52s^e	2.55s	2.58s		
	C_6D_5Br	2.47s	2.50s^c		2.58s^e	2.51s	2.54s		

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and sep = septuplet. Center of multiplet is given.
^{a} The N³-CH₃ doublet collapsed on strong irradiation at the resonance frequency of the N³−H proton. ^{b} Poorly resolved doublet. ^{c} The signal was absent in the spectrum of the corresponding S−CD₃ ester. ^{d} The solubility in CCl_4 was too low for recording the spectrum at −20 °C. ^{e} Necessarily identical for Z and E positions. ^{f} The signals from the ethyl group are ($CDCl_3$): CH₃ (Z) 1.30t, (E) 1.27t, CH₂ (Z) 3.88q, (E) 4.18q. A considerable solvent shift is observed in C_6D_5Br: CH₃ (Z) 0.91t, (E) 0.97t, CH₂ (Z) 3.42q, (E) 3.86q. ^{g} The signals from the isopropyl group are ($CDCl_3$): CH₃ (Z) 1.28d, (E) 1.22d, CH (Z) 4.92sep, (E) 6.00sep. A considerable solvent shift is observed in C_6D_5Br: CH₃ (Z and E) 0.85d, CH (Z) 4.67sep, (E) 5.98sep. ^{h} Average values from at least two measurements. The estimated error is 3 %.

rotamers. However, on cooling the signals are broadened. At -20 °C all the compounds *1*, *2*, and *4 − 6* exhibit well-resolved separate signals from the two isomers. As observed in the case of the corresponding selenium compound [1] the dithiocarbazate *3* failed to show the expected splitting of the signals at temperatures down to -40 °C. Since the rotational barriers are expected to be of the same magnitude in compounds *1 − 3* this result is taken to indicate that the population of one of the isomers of *3* is very low. The chemical shift data and the isomer ratios in four solvents are tabulated in Table 1.

In all cases the NMR spectra can be explained by assuming an equilibrium composed of the *Z* and the *E* isomers shown in Fig. 1 (Y=S). In principle, a barrier to rotation exists around both the $N^2 - C$ bond and the $C - S$ bond. However, recent CNDO/2 calculations indicate [6] that (i) the energy barrier to rotation around the $C - S$ bond is one order of magnitude lower than that around the $C - N$ bond, and (ii) hindered rotation around the $C - S$ bond leads to only one energetically favourable isomer in the case of compounds such as *1 − 6*. Empirically, a reliable indication of isomerism around the $C - S$ bond has not been observed. In the present case the *Z/E* isomer ratio varies with changes in solvent, concentration, and temperature, allowing a clear separation of the signals in two groups, each arising from one isomer. When possible, this was confirmed by spin decoupling experiments and in the case of *2* by recording the spectrum of the *S*-trideuteriomethyl ester.

In order to decide which signals arise from the *Z* and which from the *E* isomer, we chose as model compounds the cyclic dithiocarbazates shown at the top of Table 1. By virtue of their cyclic structures they of necessity have the $N^2 - CH_3$ groups situated in the *Z* position. In accordance with generalisation (3) mentioned above for the corresponding selenium compounds, the signal from this group is displaced towards higher field in CCl_4 solution relative to $CDCl_3$ solution. However, in order to obtain a more firm basis for the assignment the solvent shift was determined in the four solvents $CDCl_3$, CD_3NO_2, CCl_4, and C_6D_5Br. Since the solvent shifts of the $N^2 - CH_3$ group of the *Z* and the *E* forms in these solvents are quite different, it was possible to use this as a criterion for assigning the isomers. Furthermore, generalisation (1) stated above also applies to methyl substituted thioureas,[7] monothiocarbazic esters,[8] and thioamides.[9] The assignment given in Table 1 is in complete accordance with this rule. Finally, if the NMR spectra of the sulfur and selenium compounds corresponding to Fig. 1 are compared they show a striking resemblance in their solvent, concentration and temperature dependence. This is taken to indicate that similar factors are operative within both classes of compounds in determining the $Z - E$ isomer ratios.

Our results can be compared with those reported by Bauman [10] for thiocarbamate esters. In the case of *O*-methyl *N*-methylthiocarbamate it was demonstrated that $E - Z$ isomerism gives rise to signal splitting at temperatures below 36 °C. The assignment of *Z* and *E* isomers was based primarily on the generalization (1) mentioned above. This assignment has recently been confirmed by Bauman [11] by using the ability of tris(dipivalomethanato)europium(III) to form complex compounds selectively with the *E* form. It was furthermore shown [10] that the benzene-induced shift (*i.e.* $\delta_{CDCl_3} - \delta_{C_6D_6}$) is greater for the $N - CH_3$ signal from the *E* form than from the *Z* form. This empirical result has also been found to apply in the case of thioamides [12] and thioureas [13] and it is easily seen from Table 1 that it is in agreement with the bromobenzene shifts ($\delta_{CDCl_3} - \delta_{C_6D_5Br}$) observed for the dithiocarbamates *4 − 6*. In our opinion, therefore, the assignment given by Rao *et al.*[14,15] for *O*-methyl *N*-methylthiocarbamate and related compounds should be changed to agree with the assignment given by Bauman. Similarly, the present results suggest that the assignment made by Holloway and Gitlitz [2] for dithiocarbamates should be reversed.

The $Z - E$ isomer ratios for *1 − 3*, *5* and *6* are qualitatively the same for the corresponding sulfur and selenium compounds.[1] Both dithio- and diselenocarbamates show a small but definite tendency for the larger *N*-alkyl group to occupy a *trans* relationship to $C - SCH_3$ and $C - SeCH_3$, respectively. This trend is more marked in the case of *N*-isopropyl than in the case of *N*-ethyl groups. Since dilution experiments indicate that intermolecular forces can be neglected to a first approximation, this must

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be due either to an inductive or to a steric effect. The present results allow no distinction between these possibilities. However, it has been shown [6] that the steric requirements of the SCH$_3$/SeCH$_3$ groups are much larger than those of the double-bonded sulfur/selenium provided that rotation around the C−S/C−Se bonds is not strongly restricted. In our opinion this is the most likely explanation for the observed trend. In the dithiocarbazates the Z forms predominate. This can be explained by invoking intramolecular compensation of the local dipoles in the same way as for diselenocarbazates.[1]

The coalescence temperatures for the Z−E splitting have in all cases been found to lie between 10 and 40 °C (CDCl$_3$) while those of the selenium analogues [1] are somewhat higher (e.g. Se-methyl N^2,N^3-dimethyldiselenocarbazate in C$_6$H$_5$Br at ca. 70 °C). In agreement with earlier results [2,16] Yoder et al.[17] have determined the coalescence temperature for 4 to be 33 °C with a $\Delta G_a^{\ddagger}$ of 15 kcal/mol, while the barrier in the selenoesters has not been determined though it is undoubtedly somewhat higher. By analogy with thioamides and selenoamides [18] (cf. Walter [19]) a higher rotational barrier for the central N^2−C bond of the diselenoesters can be explained by a more extensive electron delocalisation of the NCSe group.

Tin(IV) complexes of N,N-dimethylthio, dithio-, seleno-, diseleno-, and thioselenocarbamates have been described by Tanaka et al.[20−23] In the ^{1}H NMR spectra of the tin(IV) compounds with the mixed ligands Me$_2$NCOSe- and Me$_2$NCSSe-, the methyl groups gave rise to a doublet in which one of the signals was observed to be smaller in height and broader than the other. This was explained as due to trans coupling probably of 1−2 Hz in those molecules containing the natural abundance of [77]Se. In order to test the possibility of broadening of lines by coupling to selenium, the spectra of 4 and the selenium analogue Me$_2$NC(Se)SeMe were compared in CDCl$_3$ at −40 °C in approximately identical concentrations. Within experimental error identical half-band widths were found for CH$_3$−N signals in both compounds (1.2 Hz) suggesting the coupling with [77]Se to be too small to give rise to the suggested broadening of the lines.

The infrared spectra of the compounds 1−6

are remarkably similar to those of the corresponding selenium compounds in the range 1200−4000 cm^{-1}. Below this region the change from CSS to CSeSe is followed by the systematic shift of several strong bands towards lower wave numbers. Especially prominent are peaks in the range 900−1100 cm^{-1}. Normal coordinate analyses for the dimethyldithiocarbamate [24] and the dimethyldiselenocarbamate ions [25] have shown, that bands in this region originate in highly mixed vibrations, so location of the bands with major CS/CSe stretching contributions has not been attempted. The deformational vibration of the CH$_3$ group bonded to sulfur was established by replacement with the CD$_3$ group. It occurs around 1430 cm^{-1} and when bonded to selenium around 1415 cm^{-1} in agreement with published evidence.[26] In the deuterated compounds the corresponding bands were observed in the 1000−1030 cm^{-1} range.

EXPERIMENTAL

Conditions and equipment used for the physical measurements were those described in part XI of this series.[1]

Methyl 2,3-dimethyldithiocarbazate (2). An ethanolic solution (4 ml) of methyl iodide (10^{-3} mol) was added to a filtered aqueous solution (5 ml) of potassium 2,3-dimethyldithiocarbazate [27] (10^{-3} mol). The reaction mixture was stirred for 5−10 min at room temperature and the solvent evaporated *in vacuo* with gentle heating until a volume of ½−1 ml was reached. This residue was extracted with benzene, dried, and taken to dryness. The crude product was purified by dissolution in ether and reprecipitation with pentane (−80 °C). The yield was 75 % of colourless crystals, m.p. 16.5−18 °C. (Found: C 31.91; H 6.57; N 18.70. Calc. for C$_4$H$_{10}$N$_2$S$_2$: C 32.00; H 6.71; N 18.66).

Methyl 2-methyl-2-ethyldithiocarbamate (5). Methylethylammonium chloride (40 mmol) was added to powdered potassium hydroxide (40 mmol) in dioxane (15 ml) and the mixture was stirred for 30 min. The resulting amine solution was dried (KOH pellets) and then added to a suspension of powdered KOH (40 mmol) in dioxan (40 ml). Carbon disulfide (40 mmol) in dioxan was added to the vigorously stirred solution over a period of 1 h. At the end potassium methylethyldithiocarbamate was filtered off, washed with dioxane and dry ether and dried *in vacuo*. The reaction with methyl iodide proceeded as described above for 2. The compound was purified by dissolution in the minimum amount of pentane and cooling to ca. −80 °C with scratching. The solid that separated

was quickly collected by centrifugation, washed with a small amount of cold pentane and dried *in vacuo*. The melting point was well below room temperature. Yield 60 %. (Found: C 39.49; H 7.26; N 9.82. Calc. for $C_5H_{11}NS_2$: C 40.24; H 7.43; N 9.38). Though the analysis was not quite satisfactory, the impurities were not discernible in the NMR spectrum.

Methyl 2-methyl-2-isopropyldithiocarbamate (6). The compound was prepared as was the previous compound, except that it was found necessary to add a small amount of water during the generation of the amine. Yield 50 % of a colourless oil, which solidified by immersion in a bath cooled to *ca.* − 80 °C. (Found: C 44.30; H 8.20; N 8.56. Calc. for $C_6H_{13}NS_2$: C 44.13; H 8.02; N 8.58).

The preparation of the cyclic dithiocarbazates has been described in a previous communication.[28] The structures have been established by comparison of the spectral properties with those of the corresponding selenium compounds.[29]

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