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NMR STUDY OF SOME DERIVATIVES OF DITHIOCARBAZIC ACIDS

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Abstract—The NMR spectra of a series of methyl and phenyl derivatives of dithiocarbazic acid have been examined. The value of the chemical shift of the S–Me group is found to be 2·3–2·6 ppm, while for N^2-Me and N^3-Meδ is in the range 3·4–3·6 ppm, and 2·4–2·7 ppm, respectively.

Present data suggest that the rotation about the SC–N and SC–S bonds is sterically hindered.

INTRODUCTION

An extended research programme on metal complexes of dithiocarbazic acid and its derivatives has been reported since 1970.[1-5] The ligands and the complexes have been characterized by elemental analysis, molecular weight, conductivity measurements, electronic and vibrational spectra and determination of magnetic moments.

More recently some Ni(II) complexes and the corresponding methyl esters of the ligands have been studied by means of X-ray photoelectron spectroscopy.[4]

On the other hand, very little is known about the NMR characteristics of both the ligands and the complexes. Values of chemical shift of some Me-substituted dithiocarbazic acids or sulfides are reported by Anthoni *et al.* The isomerism of N,N-diisopropyldithiocarbazic esters has been investigated by NMR spectroscopy.[7] As far as complexes are concerned as only the NMR spectrum of Ni(II)-bis (2-methyl) dithiocarbazate is reported,[1] we have undertaken a systematic PMR study of these ligands and complexes. In this paper we report the results obtained for the free ligands.

EXPERIMENTAL

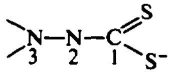
Compounds **1**, **2**, **3**, **4**, **8**, and **10** of Table 1, have been prepared following literature procedures.[8-11]

Compounds **5**, **6**, **7**, **9** although not yet reported have been a kind gift from Drs A. Monaci and F. Tarli.[12] The formula **11** has been confirmed by elemental analysis, determination of molecular weight and IR spectra.

Deuterated Merck UVASOL solvents have been used for NMR measurements. TMS has always been added as reference and for field stabilization. The PMR spectra have been recorded with a Bruker HX-90 spectrometer. A scale expansion of 20 Hz/cm has been generally used in recording the spectra and the uncertainty on the frequency determination has been estimated ±2Hz, except in the case of broad resonances, when the uncertainty is obviously larger (and reported in the Table).

RESULTS AND DISCUSSION

Several derivatives of dithiocarbazic acid have been examined. The position of the substituents on the acid skeleton will be indicated following the IUPAC convention:

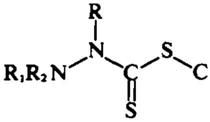


The NMR data relative to the compounds examined are reported in the Table.

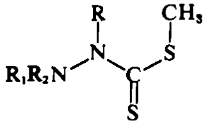
From the data, it may be noted that the chemical shift of the S–Me group is essentially constant and independent of the rest of the molecule ($\delta = 2{\cdot}45 \pm 0{\cdot}15$ ppm in DMSO and in chloroform solutions).

The type of compound under investigation can exhibit conformational isomerism, due to hindered rotation about the partially double SC-N and SC–S bonds.

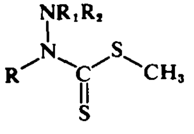
Four planar conformers can be expected



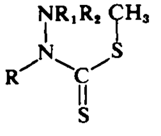
cis-cis **A**



cis-trans **B**



trans-cis **C**



trans-trans **D**

As in compounds **1** and **2**, the spectra show a splitting of the NH$_2$ resonance even at room temperature,* we have recorded variable tempera-

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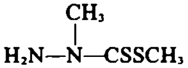
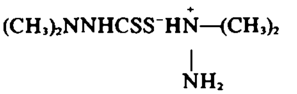
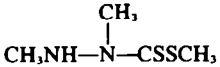
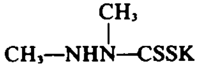
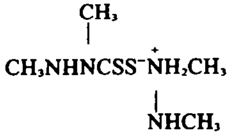
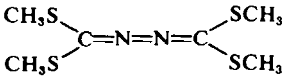
*The S–Me resonance of **1** in DMSO is also split under these conditions.

Table 1. PMR spectra of dithiocarbazic acid derivatives (magnet temperature; TMS internal reference, $\nu_0 = 90$ MHz)

Compound	Solvent	N^3-R (R=CH_3, C_6H_5) δ (ppm)	N^3-H δ (ppm)	N^2-R (R=H or CH_3) δ (ppm)	S–CH_3 (or S–H) δ (ppm)	N^+–CH_3 δ (ppm)
$H_2NNHCSSCH_3$ **1**	$CDCl_3$		5·00 ± 0·15 4·5 ± 0·1	8·97 ± 0·09	2·60^{sh+}	
	DMSO		7·8 ± 0·2 5·2 ± 0·2	10·74	2·39 2·32	
 $H_2N-\overset{CH_3}{N}-CSSCH_3$ **2**	$CDCl_3$		5·52 4·37	3·55	2·57	
	DMSO		5·54	3·59	3·33	
$(CH_3)_2NNHCSSCH_3$ **3**	$CDCl_3$	2·63		8·71 ± 0·03	2·54	
	DMSO	2·50		10·81	2·36	
 $(CH_3)_2NNHCSS^{-}\underset{NH_2}{\overset{+}{H}N}-(CH_3)_2$ **4**	DMSO	2·43		7·67^{a}		2·72
 $CH_3NH-\overset{CH_3}{N}-CSSCH_3$ **5**	DMSO	2·51^{d}	5·71^{q}	3·51	2·33	
 $CH_3-NH\overset{CH_3}{N}-CSSK$ **6**	DMSO	2·40^{d}	7·40^{q}	3·46		
 $CH_3NH\overset{CH_3}{N}CSS^{-}\underset{NHCH_3}{\overset{+}{N}}H_2CH_3$ **7**	DMSO	2·44	4·96^{a}	3·47		2·64
ØNHNHCSSCH$_3$ **8**	$CDCl_3$	7·04^{c} ± 0·04	6·03	8·70 ± 0·04	2·58	
	DMSO					
Ø$_2$NNHCSSCH$_3$ **9**	$CDCl_3$	7·20^{c}		9·52	2·53	
	DMSO	7·21^{c}		11·12	2·46	
Ø$_2$NNHCSSH **10**	$CDCl_3$	7·20		9·26	4·0 ± 0·2	
	DMSO	7·22		12·70 ± 0·03	*	
 $(CH_3S)_2C{=}N{=}N{=}C(SCH_3)_2$ **11**	$CDCl_3$				2·52 2·45	
	DMSO				2·46 2·43	

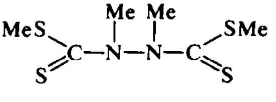
^{a} = all NH protons + HOD; ^{d} = doublet; ^{c} = center of multiplet; $^{sh+}$ = shoulder to high field; ^{q} = quartet; *exchanges with water ture NMR spectra of these and similar compounds to investigate their conformational equilibria. The results of the complete kinetic study based on total line-shape analysis will be given in detail in a subsequent paper. We anticipate here only one main conclusion, i.e. that only two isomers of **1** and **2** can be detected in chloroform solutions even at low temperature (220°K).*

The isomer ratio changes somewhat with temperature, but oscillates around 50:50 for both **1** and **2**.

We tentatively assigned the two signals to conformers A and C, by analogy with similar compounds, like thioureas[13] and especially thiocarbamate esters;[14] the experimental results relative to these latter compounds[14] suggest that the O–Me group is always *cis* to the thioamide S atom.† The question, however, needs further discussion and we are presently interested in the semiempirical quantum-mechanical calculations of the most stable conformations of our esters.

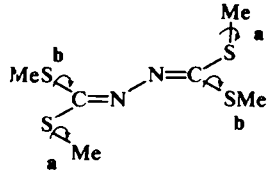
The NMR spectrum of the compound $[H_2N-N(CH_3)-CSS]_2$ is reported in the literature[6] (chemical shifts in DMSO solutions: N^2-CH_3 3·60 ppm, N^3-H 5·58 ppm). The chemical shifts are in good agreement with the values found for **2**, but the authors[6] do not mention any splitting of the resonances due to conformational isomerism in solution.

The room temperature spectra of **11** also show two sharp singlets for the Me groups both in chloroform and DMSO solutions. The chemical shift of these resonances corresponds to the values found for S–Me groups, thus ruling out structures like



which should exhibit the N–Me resonance at *ca* 3·5–3·6 ppm.

The C═N—N═C skeleton should be planar because of delocalization of π electrons. Space-filling models show that only the *trans* isomer is sterically permitted and, even in this form, free rotation of the four–SMe groups about the C–SMe bond is impossible. Two–SMe groups, indicated in the formula below as **b** can rotate freely, while the **a** groups are in fixed positions relative to and slightly out of the C═N—N═C plane to allow free rotation of the -Me group.



This steric arrangement accounts for the two resonances found in the NMR spectrum. We may *tentatively* assign the resonance at $\delta = 2{\cdot}52$ ppm in $CDCl_3$ to the freely rotating groups, by comparison with the values obtained for similar groups (Table 1).

From the δ values reported in Table 1, it appears that N^2–H is less screened than N^3–H. This finding is in agreement with the results obtained for some dithiocarbazic esters by ESCA studies;[4] in fact, the experimental data suggest a higher negative charge on N^3 than on N^2 and this finding is supported by semiempirical quantum-mechanical calculations of the charge distribution in the molecules examined. The shift to lower field observed for the N^2–H proton in compounds **1** and **3**, going from chloroform to DMSO solutions, can safely be ascribed to H-bonding to the solvent.

In the case of hydrazinium salts **4** and **7**, all the NH protons, together with the HOD present in the solvent, give rise to only one broad resonance; a fast exchange of protons among the different sites may be supposed.

According to the data reported by Evans and Kynaston[15] on the protonation of hydrazine derivatives, we may assume that in the case of **4** protonation occurs on the substituted N atom of the hydrazinium cation, while the two N atoms are undistinguishable in the case of **7**. A shift to low field is to be expected for the N-Me resonance upon protonation at the N atom, by analogy with the behavior of methylamine.[16,17] Moreover, the chemical shift of the N-Me group of 1,2-dimethylhydrazine in DMSO solution is 2·37 ppm, whereas the corresponding hydrochloride has the Me resonance at 2·64 ppm. We may therefore assign, with reasonable confidence, the resonance at 2·72 ppm to the $\overset{+}{H}NMe_2$ group in **4** and the signal at 2·64 ppm to the $^{+}NH_2Me$ group in **7**. This resonance has an integrated intensity of 2 relative to the other two Me resonances (integrated intensities 1:1). A possible explanation is that, given the equivalence of the two N atoms of the cation moiety, the proton exchanges rapidly its position between the two sites giving rise to only one resonance.

Compounds **5** and **6** give rise to very simple and clear-cut spectra. The N^3–Me resonance is a sharp doublet with a coupling constant to the N^3–H proton of 5·7 ± 0·1 Hz, in the case of **5**, and 6·1 ± 0·1 Hz for **6**. The N^3–H resonance appears as a clear quartet slightly broadened by the quadrupole effect of nitrogen. The N^2–Me peak is a sharp singlet, as is the resonance of the S–Me of **5**.

In the paper by Anthoni *et al.*[6] the NMR spectrum of $(MeNH-N(CH_3)CSS)_2$ is reported. They give the following values for δ in DMSO: 3·52 for

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*Indeed, all the resonances of **1** and **2** are split in two in the low temperature region.

†We assume then that the same conclusion holds in the case of our S–Me esters.

N^2-Me, 2·65 for N^3-Me and 6·1 for N^3-H; they give also a value for J_{CH-NH} of 6·0 Hz. The agreement between their data and ours for the very similar compounds **5** and **6** seems rather satisfactory. The differences in the N^3-H chemical shift are not surprising since this resonance should be temperature and concentration dependent, because the proton is certainly involved in H-bonding to the solvent.

Compounds **8** and **9** show complex resonances in the aromatic region. In the case of 3-phenyl-S-methyldithiocarbazate (**8**), the phenyl resonance appears as one multiplet centered around 7·26 ppm and another centered around 6·87 ppm, of relative integrated intensities 2:3. The low-field group of resonances may be assigned to the ortho protons, while the second group is ascribable to meta and para protons. For compound **9** such a distinction is not possible.

Compound **10**, in DMSO solution, shows a shift to low field of the N^2-H resonance relative to the ester **9**; otherwise the signals are essentially in the same position, both in chloroform and in DMSO, though somewhat broadened. The frequency of the SH resonance is undefined in DMSO, because there is an immediate and very fast exchange with the water present in the solvent. The –SH resonance is very broad also in $CDCl_3$ solution.

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