N-Isothiocyanatoamines

IX. Infrared Study by Deuterium Labelling of an N-Isothiocyanatodimethylamine Dimer and Analogous Compounds Containing the 1,2,4-Triazole Ring. Identification of the C=S Stretching Frequency of Tertiary Cyclic Thioureides

UFFE ANTHONI, CHARLES LARSEN and
PER HALFDAN NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen,
The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The infrared spectra of dimeric N-isothiocyanatodimethylamine, 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione, and seven deuterated species have been recorded. The results permit the absorption arising from internal vibrations of the methyl groups to be selected leaving a total of sixteen bands to be assigned to vibrations of the remaining system. A tentative assignment of these bands is proposed on the basis of further comparison with a series of related triazole and hydrazine derivatives. Contrary to what is commonly assumed, it is concluded that the C=S stretching motion is not restricted to one or two bands. It is shown that a more realistic viewpoint involves the assumption that extensive coupling with other vibrations occurs. In support of this view only small changes are produced in the spectrum when selenium is substituted for sulfur in a related triazolinethione.

In an earlier paper[1] we have demonstrated that the dimerization of N-isothiocyanatodimethylamine proceeds via dipolar intermediates to give 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione (II). The proof for the structure was based primarily on the fact that a reaction sequence involving methylhydrazine and 1,1-dimethylhydrazine also furnished II by way of 1,1,4-trimethylthiocarbonohydrazide and the thiol (I).

The deuterated mono- and dimethylhydrazines have recently[2] been made available from direct deuteriomethylation of hydrazine. By reactions analogous to those outlined above they were converted in good yield[3] to the deuterium labelled analogues of I and II. The structure and spectrum of
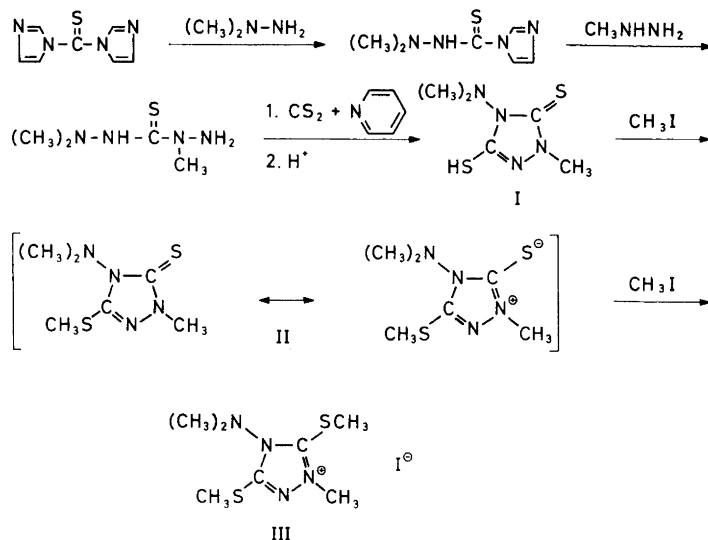
the intermediate 1-(N,N-dimethylthiocarbazoyl)imidazole has been inves-
tigated in connection with other thiocarbazoylimidazoles [4] and the infrared
spectra of the 1,1,4-trimethylthiocarbonohydrazides will be treated in full in
a forthcoming series of papers dealing with thio- and selenocarbonohydrazides.[5]
The symbolism used for describing the deuterium labelled derivatives of I,
II, and IV is summarized in Table 1.

Table 1. The suffices used to indicate the groups deuterated in I and II.

Deuteration of	Suffix
SH	S-d_1
SCH$_3$	S-d_3
NCH$_3$	N-d_3
N(CH$_3$)$_2$	N-d_6
NCH$_3$ and N(CH$_3$)$_2$	N-d_9

Only very little is known of the characteristic infrared absorption of 1,2,4-
triazole and its derivatives. Most of the data in this field have been summarized
by Dziewonska,[6] who examined a series of differently substituted 1,2,4-triazoles
and analyzed the patterns obtained. It appears, that in 1,2,4-triazolinethiones
analogous to I and II there is still considerable doubt whether the C=S
stretching vibration gives rise to a band near 1100 cm^{-1}, near 1300 cm^{-1},
or near 1500 cm^{-1}. A similar disagreement for thioureides has recently been
settled [7] in favour of a location of the C=S stretching absorption below 800
cm^{-1}. An exception was found in the case of tertiary thioureides for which

this band occurs at higher frequencies though in no case higher than 1000 cm^{-1}. From the point of view that I and II are (cyclic) tertiary thioureides these results indicate assignments of C=S stretching vibrations to peaks in the regions around 1300 or 1500 cm^{-1} to be rather unlikely. On the other hand it should be pointed out that the evidence cited refers only to acyclic thioureides and there is no safe way of judging *a priori* how the force constant changes when the C=S group is incorporated in a heteroaromatic ring as in I or II. To elucidate this problem a series of compounds related to I and II were prepared and their infrared spectra recorded for comparison. The methiodide of II (III) was prepared following the reasoning that the enhanced single-bond character of the CS bond in III relative to II should be associated with a shift of the corresponding stretching band towards lower frequencies. Examination of methiodide derivatives turned out to be a useful diagnostic test for the C=S character of bands in acyclic thioureides.[7] Furthermore, the 3:2 complex (IV) of II with copper(I) chloride and the seven methyl deuterated species were prepared. The infrared spectrum of IV indicates that II functions as a bidentate ligand with bond formation to the (CH$_3$)$_2$N and the CS groups. Owing to the small solubility of IV in all types of solvents the molecular weight could not be determined but a structure with sp^3-hybridized copper bridged with chlorine seems the most probable. It should be noted that the influence of complex formation with copper(I) chloride on the bands with CS stretching character in the spectrum of tetraethylthiourea, which is the only case so far investigated for tertiary thioureas, is small and irregular.[7] Accordingly the results obtained with IV should be used with caution in this respect.

Selenium analogues have proved extremely valuable for locating bands with CS character in the case of acyclic thioureas. An attempt was therefore made to prepare the selenium analogue of (I) by treating 1,1,4-trimethylseleno-carbonohydrazide [5] with carbon disulfide and pyridine. However, it was only possible to isolate a 90 % yield of the pyridinium salt of (I) from the reaction mixture and it seems necessary to conclude that an exchange of selenium with sulfur occurs under these conditions. This unusual reaction is at present being investigated in this laboratory but attempts to prevent this exchange have so far been unsuccessful. Instead, 1,3,4-trimethyl-1,2,4-triazole-5-ine-thione (V) and the selenium analogue (VI) which have structures closely related to II, were prepared. Such compounds will be the subject of a forthcoming paper from this laboratory.[8]

V . X = S
VI . X = Se
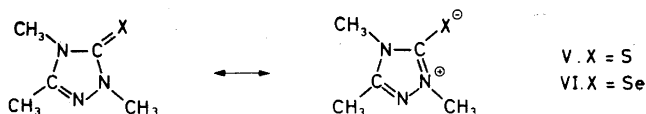
The infrared absorption bands to be discussed may conveniently be divided into two groups. In Table 2 the bands arising primarily from internal vibrations of the three different kinds of methyl groups are listed. For each band the mean value and the maximum deviation are given. All these bands

Table 2. Infrared absorption (KBr, cm⁻¹) of methyl groups in I, II, and IV.[a]

Vibration	Group	I CH_3	I CD_3	II CH_3	II CD_3	IV CH_3	IV CD_3
ν(C–H)/ν(C–D)	CH_3S/CD_3S	— ; —	— ; —	3005w ±5; 2920w ±5	2254w ±5; 2121w ±5	2916w ±5	2130w ±5
	CH_3N/CD_3N	2935w–m ±5; 2872w ±10	2126vw ±5; 2107vw ±5; 2058vw ±5	2937m ±5; 2854w ±10	2120w ±5; 2096vw ±5; 2058vw ±5	2937vw ±5	2146vw ±5; 2111vw ±5; 2058w ±5
	$(CH_3)_2N$/$(CD_3)_2N$	2990m ±3; 2965m ±3; 2943m ±3; 2903m ±3; 2830vw ±5; 2795vw ±5; 2783vw ±3	2236m ±3; 2223m ±3; 2179w ±3; 2131w–vw ±3; 2107w ±3; 2088w ±3; 2075w–vw ±3; 2062m ±3	2992m ±3; 2964m ±3; 2936m ±3; 2900m ±3; 2828vw ±3; 2794vw ±3; 2777vw ±3	2236w ±3; 2217m ±3; 2175vw ±3; 2130w ±3; 2105vw ±3; 2086w–vw ±3; 2076w–vw ±3; 2060m ±3	2946w–m ±5; 2905w–vw ±5; 2865w–vw ±5	2278vw ±3; 2249vw ±3; 2156vw ±3; 2118w ±3; 2057w ±3
$\delta(CH_3)$/$\delta(CD_3)$	CH_3S/CD_3S	— ; —	— ; —	— ; —	1033w ±1; 1014vw–m ±1	1431w ±2	1043w ±1; 1006w
	CH_3N/CD_3N	1461m ±2; 1392m–s ±2; 1347w ±4	1105w–vw ±1	1461m ±1; 1355m ±3	1090w ±5	1449w ±4; 1412m ±1	1055m ±1; 1040m ±7
	$(CH_3)_2N$/$(CD_3)_2N$	1481m–w ±1; 1443m–s ±5	1180m ±3; 1177m ±11; 1073m ±1; 1047m ±2	1471w ±2; 1445m–s ±5	1180m ±7; 1164w–m ±12; 1067w–m ±2; 1048w–m ±2	1458s ±1	1183vw ±5
$\varrho(CH_3)$/$\varrho(CD_3)$	CH_3S/CD_3S	— ; —	— ; —	992w–m ±2	772w ±5; 742vw ±1	985w ±3	770w ±5
	CH_3N/CD_3N	1076m ±7	853m ±1	1073m ±8	853w ±4	1148m ±15	872w ±3
	$(CH_3)_2N$/$(CD_3)_2N$	1213w–s ±4; 1185w–m ±15; 1150s ±1; 1131w	950m ±3; 836m ±1; 818m ±1	1209w–s ±2; 1185w–m ±15; 1145m ±1; 1129w ±1	940m ±1; 835w–m ±1; 824w ±4; 816w ±1	1239w ±2; 1186w ±3; 1104w–m ±6	848w ±2; 828w ±5

[a] The following abbreviations have been used: ν = stretching vibration, δ = deformation, and ϱ = rocking. The intensity of the bands is denoted by: vs = very strong, s = strong, m = medium, w = weak, and vw = very weak.

were adequately defined by comparison of the spectra of undeuterated com-
pounds with the spectra of the corresponding deuterated compounds. The
remaining skeletal frequencies, S_1-S_{16}, are collected in Table 3 and are
generally only very little influenced by deuteration of the methyl groups.
Assignments for the individual bands were attempted mainly on the basis
of comparison of the spectra of I—IX.

From Table 2 it can be seen that most of the absorption pattern in the
range from 2700 to 3000 cm^{-1} in the spectra of I and II originates from the
methyl groups of the dimethylamino grouping. The recorded bands for IV
show that the intensity of the absorption, especially in the low-frequency
region, is strongly influenced by the presence of coordinated copper(I) chloride.
Since observation of low-frequency bands from the dimethylamino group
in this region is known [2,9] to be intimately associated with the presence of an
unshared electron pair on the neighbouring nitrogen atom these results support
the formulation of the chelate (IV) given above, *i.e.* with coordination to the
dimethylamino group. The other methyl groups display $\nu(C-H)$ stretching
absorption too weak to substantiate without recourse to the deuterated
analogues.

The location of the bands attributed to deformation or rocking motions
of the methyl groups joined to nitrogen show only insignificant deviations
from I to II. Since the same holds for most of the skeletal vibrations (Table 3)
we may conclude that (I) occurs exclusively as the thiol form. This is substan-
tiated by the occurrence of a band due to the $\nu(S-H)$ stretching vibration
in (I) and its methyldeuterated analogues at 2526 cm$^{-1}\pm1$ (m), and the cor-
responding band arising from the $\nu(S-D)$ vibration in I—S—d_1 at 1849
cm^{-1}. The adoption of the thiol form by (I) is obviously a result of the stabiliza-
tion by resonance analogous to that in the case of II. This similarity between
I and II also allows the bands arising from the methyl group bonded to sulfur
to be picked out readily. An exception is the band expected from the $\delta(CH_3)$
deformation vibration which obviously is obscured by the other strong absorp-
tion in the region between 1400 and 1500 cm^{-1}.

If the mass of the methyl groups is thought of as concentrated in single
points a total of 30 skeletal vibrations is calculated for I and II. If both
molecules are further approximated by C_s symmetry we find that 21 of these
are in-plane vibrations, and that only 12 will have prevailing bond-stretching
character. Though this is admittedly a very crude description it is probably
the most useful point of view from which molecules as I and II can be con-
sidered. From results obtained for other five-membered heterocyclic rings [10]
it can be inferred that the in-plane vibrations of the bond-stretching type
will give rise to bands situated within the range covered by the headings
S_1-S_{13} in Table 3. These bands will be the main subject of the following
discussions since the CS stretching band would be expected to occur here.

The S_{10} band (Table 3) is only weak, but of interest as the most obvious
feature distinguishing I from II, III, and IV. Furthermore, this band is not
observed in the cases where the CH$_3$S group is deuterated. If we assume the
reason for this to be a shift of S_{10} towards lower frequencies, *i.e.* that it becomes
indistinguishable from S_{11}, then we can assign S_{10} to the CH$_3$—S stretching
vibration. It is in the upper end of the range commonly quoted for this

Table 3. Infrared absorptions (KBr, cm⁻¹) of

Compound	Labelling	S_1	S_2	S_3	S_4	S_5	S_6
I	None	1502s	1462	1366m	1322s	1272w	1019m
	$S-d_1$	1500s	1460s	1362m	1320s	1271w	1019m
	$N-d_3$	1502s	1414s	1367m	1321s	1250w	1037m
	$N-d_6$	1500s	1451s	1366m	1324s	1252m	—
	$N-d_9$	1500s	1428vs	1367m	1320s	1250m	1038s
II	$N-d_0-S-d_0$	1497s	1460m	1383vs	1323vs	1274w	1020m
	$N-d_0-S-d_3$	1496s	1462m	1382vs	1325vs	1274w	1019m
	$N-d_3-S-d_0$	1499s	1416vs	1382vs	1328vs	1268w	1017s
	$N-d_3-S-d_3$	1497s	1413vs	1381s	1328vs	1257w	1017s
	$N-d_6-S-d_0$	1499s	1452s	1388s	1324s	1270m	—
	$N-d_6-S-d_3$	1495vs	1450s	1386s	1328s	1260m	—
	$N-d_9-S-d_0$	1499s	1425vs	1385vs	1321s	1255m	1037m
	$N-d_9-S-d_3$	1495s	1423vs	1382s	1322s	1253m	1038m
III	$N-d_0-S-d_0$	1516s	1485vs	—	1312s	1276m	1013m
IV	$N-d_0-S-d_0$	1520s	1488vs	1392s	1313s	1257m	1006m
	$N-d_0-S-d_3$	1520s	1485vs	1394s	1317s	1259m	1007m
	$N-d_3-S-d_0$	1507s	1484vs	1393s	1315s	1247w	—
	$N-d_3-S-d_3$	1508s	1484vs	1393s	1316s	1248w	1005m
	$N-d_6-S-d_0$	1520s	1486vs	1393s	1315s	1255m	1007m
	$N-d_6-S-d_3$	1520s	1484vs	1393s	1319s	1256m	1008m
	$N-d_9-S-d_0$	1514s	1481vs	1393s	1315s	1242m	1025m
	$N-d_9-S-d_3$	1513s	1481vs	1393s	1317s	1242m	1025m

^{a} For abbrevations see Table 2.

band [11] but close to the position proposed for other 1,2,4-triazolethioles.[6] Otherwise the spectra of I and II are very similar with the maximal shift of the other skeletal bands only of the order of 20 cm⁻¹ (for S_3).

Methylation of II to III is accompanied by the following sizable changes in the infrared spectrum: S_1 and S_2 are shifted by 20—25 cm⁻¹ towards higher frequencies and S_4, S_9, S_{14}, S_{15}, and S_{16} by 10—25 cm⁻¹ towards lower frequencies. In our opinion this indicates strongly that no band is present in II which can reasonably be assigned to an approximately pure CS stretching motion, since such a band would be expected to suffer a much greater shift on S-methylation. On the other hand the result is not decisive in this respect when it is taken into account that the CS bond in II, because of the resonance stabilization, might effectively be rather close to a single bond. If this is the case a much smaller shift is predicted on S-methylation. By assuming S_1-S_4 to originate mainly from skeletal stretching vibrations of the triazole ring (*cf.* a recent discussion of the corresponding bands of pyrazole [12]) the small shifts of S_1, S_2, and S_4 are understandable as a result of the changes in double bond character induced by methylation. (The reason for not observing S_3

I—IV due to skeletal vibrations S_1-S_{16}.[a]

S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}
989m	923w	800s	—	680m	643w	620w	584m	545w	421m
988m	923w	799s	—	681m	642w	569w	583m	544w	420m
1019s	921w	777s	—	681m	641w	618w	564m	527w	421m
992s	—	783s	—	677m	645w	606w	572m	528w	418m
1011m	—	763s	—	676m	641w	603w	548m	511w	416m
979m	923w	806s	707vw	684m	644w	635m	597m	552m	437vw
985m	924w	808s	—	684m	644w	628m	595m	549m	433vw
1010ssh	923w	781s	708vw	682m	639w	634m	575m	532m	434vw
1012ssh	922w	787s	—	683m	640vw	629m	572m	529m	427vw
980m	—	785s	708vw	678m	644vw	621m	583w	535m	432w
986m	—	786s	—	678m	644vw	617m	580w	532m	425w
1011s	—	766s	706vw	677m	640vw	617m	559w	517m	428w
1008s	—	774m	—	677m	639vw	614m	556w	515m	423w
976m	926m	791m	707vw	688m	—	640m	571w	532w	422w
992m	911m	793m	712w	675m	—	670m	584w	543w	467w
993m	913m	796m	—	675m	—	665m	583w	542w	467w
990m	911m	770m	712w	675msh	—	670m	564w	527w	465w
993m	913m	771m	—	675m	—	664m	561w	527w	463w
983m	—	771m	712w	670m	—	636m	576w	529w	443w
980w	—	777m	—	670m	—	631m	573vw	530w	437w
987m	—	757m	711w	670m	—	633m	553w	515w	442w
978w	—	754m	—	669m	—	630m	549w	513w	435w

is obscure; compare to IV below). This leaves S_9 as the most reasonable alternative for the band with the greatest CS stretching character. In our opinion $S_{14}-S_{16}$ are at too low frequencies for such an assignment, but rather are deformation bands. It appears from this discussion that S_9 is the closest counterpart to the "G band" of acyclic tertiary thioureides [7] we can find, *i.e.* it is attributed partly to the stretching motion of the CS bond as influenced by thioureide resonance as shown above. The changes of S_1-S_4, S_9, $S_{14}-S_{16}$ in II on complex formation (IV, Table 3) are qualitatively similar to those induced by S-methylation except that S_{16} now is displaced towards higher frequencies and S_3 appears with the expected position and strength.

Some of the other absorption can be tentatively assigned to skeletal vibrations on the basis of the results listed in Table 3. Deuteration of the thiol group in (I) influences the S_{13} band strongly, but leaves the other bands unaffected. Since it is in the correct range for C—S stretching vibrations it is assigned to the C—SH stretching vibration. Deuteration of the dimethylamino group in I, II, and IV gives rise to an (unclarified) displacement of S_6. This band is therefore assigned either to the C—N stretching vibrations of this

group or to the N—N stretching vibration of the bond connecting this group to the triazole ring. By deuteration of the methyl group connected with a nitrogen atom of the triazole ring, we observe S_2 and S_7 to be shifted in opposite directions in the spectra of I and II, but no corresponding shifts in the spectrum of IV. This can be explained by assuming S_7 to originate mainly from the corresponding N—CH_3 stretching motion[2] coupled with the S_2 vibration. On deuteration the band due to N—CD_3 stretching will of course be displaced towards lower frequencies, but if the coupling with S_2 at the same time diminishes, the net effect might very well be precisely the observed shifts of S_2 and S_7.

Essentially similar conclusions were obtained by inspection of the infrared spectra of V and VI. The spectra were virtually superposable in the whole range between 1200 and 1600 cm^{-1} showing that the coupling of the triazole ring vibrations with the CS (or CSe) bond is negligible. This result is consistent with the explanation set forth above, that the shift of S_4 towards lower frequencies on S-methylation is due to changes in double bond character of the triazole ring rather than CS character. The absorption of V (and that of VI given in parenthesis) in the frequency range 400—1200 cm^{-1} is the following (KBr, in cm^{-1}): 1132 (1120), 1061 (1069), 1048 (1044), 1016 (1015), 990 (988), 846, (840), 682+678 (679), 648 (646), 614 (610), 543 (534), and 494 (no counterpart). Essentially the same frequencies were measured when the spectra of V and VI in CS_2 were recorded. In this case it seems rather meaningless to talk about a CS stretching band but if such an assignment is made then the choice of the strong band at 1132 cm^{-1} in V may be preferred because of the shift (12 cm^{-1}) introduced by substituting selenium for sulfur. The band at 494 cm^{-1} in V is again at too low frequency for such an assignment, but is probably due to an NCS deformation mode.[7] Another interesting feature of V and VI is that they both exhibit the highest band from the triazole ring stretching vibrations at 1577 cm^{-1} which is considerably higher than the S_1 band (not above 1520 cm^{-1}). Part of the explanation is undoubtedly that the electronic delocalization is more extended in I and II than in V and VI. This would tend to equalize the differences in double bond character of the triazole ring in I and II relative to V and VI and thereby explain the position of the S_1 band. It is consistent with this idea that the dimethylamino group in II is not protonated even by concentrated hydrochloric acid, *i.e.* resonance structures involving this group have considerable weight as distinct from the situation with V and VI.
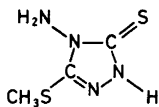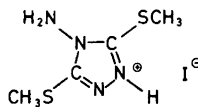

VII   VIII

Two other 1,2,4-triazole derivatives, VII and VIII, differing from II and III, respectively, only by having hydrogen attached to two nitrogen atoms instead of methyl groups, showed qualitatively the features expected

in the infrared spectra. In VII, for example, a strong band was observed at 1604 cm^{-1} attributed to the NH$_2$ deformation vibration. The same band was found in the spectrum of VIII at 1614 cm^{-1} demonstrating the nitrogen atoms of the ring to be more basic than that of the amino group. This is consistent with the above proposal for II that considerable charge from the exocyclic nitrogen atom has entered the triazole ring. This is also obvious from a consideration of the N—H stretching region in the spectrum of VIII, where the bands originating from the amino group were located at 3266 and 3160 cm^{-1} and those from the protonated ring appeared as a strong, broad absorption between 2500 and 2900 cm^{-1}. Analogous to the findings for II and III we also found VII and VIII to show only intensity and not frequency changes in the regions between 700 and 1350 cm^{-1}. Exceptions were, of course, the bands connected with the NH deformation vibration at 888 cm^{-1} in VII but at 748 cm^{-1} in VIII. Peaks with characteristics corresponding to an origin in the CS stretching vibration were not present.

$$(CH_3)_2N$$
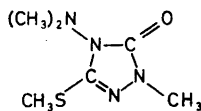
IX

In the case of acyclic thioureides substitution of sulfur with oxygen led to a complete change in the infrared spectra thereby rendering them useless for purposes such as localizing bands with CS character. On the other hand replacement of sulfur with selenium essentially only changed such bands.[7] In the hope that oxygen substitution would prove of some value for a cyclic thioureide such as II we prepared the oxygen analogue IX. The triazole ring vibrations still gave rise to four bands analogous to S$_1$—S$_4$ and situated at 1516, 1481, 1407, and 1289 cm^{-1}, respectively, which compare favourably with the positions in the case of II. We were not able to locate S$_5$ with certainty, but somewhat unexpectedly S$_6$—S$_8$ were found within only ± 10 cm^{-1} from the frequencies given for II in Table 3. This seems to substantiate that they are mainly due to substituent vibrations as proposed above for S$_7$ and S$_8$. The most interesting feature is perhaps that S$_9$ was shifted from 806 cm^{-1} in II to 878 cm^{-1} in IX. This is consistent with the assumption that S$_9$ is indeed the band with the greatest CS strechting character and suggests that oxygen analogues will perhaps be of more value in identifying this type of vibrations in cyclic thioureides than would be expected from previous work.

EXPERIMENTAL

Copper(I) chloride complex of II (IV). To a solution of II in absolute ethanol, a solution of copper(I) chloride in concentrated hydrochloric acid was added in various proportions. Cooling for a short time was sufficient for inducing crystallization of the ochrebrown complex, m.p. 238—240°C (decomp.) in nearly quantitative yield. Independent of the relative amounts of ligand and metal halide used, in the complex the proportion was always 2:3. (Found: C 20.58; H 3.47; N 15.85. Calc. for $C_{12}H_{24}Cu_3Cl_3N_8S_4$: C 20.42; H 3.43; N 15.88).

Reactions between 1,1,4-trimethylselenocarbonohydrazide [5] *and carbon disulfide.* A solution of the selenocarbonohydrazide (230 mg) and carbon disulfide (170 mg) in pyridine (4 ml) was boiled for 1 h. After the components were mixed a deep red colour rapidly at the upper end developed, and during the reaction a strong smell of hydrogen selenide became apparent of the refluxed condenser. The reaction mixture was allowed to cool and dried *in vacuo*. The residue was dissolved in water and extracted with ether. By addition of hydrochloric acid to the water phase a colourless compound separated which was shown by melting point, mixture melting point, and infrared spectroscopy to be identical with II. The yield was higher than 90 %.

4-Amino-3-methylthio-1,2,4-triazol-2-ine-5-thione (VII). This compound was prepared according to the instructions given by Sandström.[13] The methyl group was apparent in the NMR spectrum (in dimethylsulfoxide-d_6) by a singlet at $\tau = 7.52$ ppm which is at nearly the same position as for the corresponding group in II (7.50 ppm).[1] The signal from the amino group was observed as a rather broad band at $\tau = 5.2$ ppm and the signal from the hydrogen atom bonded to the triazole ring also rather broad at $\tau = -3.3$ ppm.

Methiodide of VII (VIII). To a suspension of VII in an excess of methyl iodide was added, in small portions, boiling ethanol until VII had dissolved completely. The solution was filtered, and after standing for some time an 88 % yield of colourless, crystalline VIII, m.p. 183—186°C (decomp.) was obtained. (Found: C 15.80; H 3.04; N 18.36. Calc. for $C_4H_9IN_4S_2$: C 15.79; H 2.98; N 18.42). Only one signal was observed in the NMR spectrum (in dimethylsulfoxide-d_6) from the methyl groups and had the value $\tau = 7.33$ ppm, which compares favourably to the mean value of 7.25 and 7.29 ppm found for the corresponding groups in III.[1] By addition of aqueous sodium hydroxide to VIII, colourless crystals of *4-amino-3,5-bis(methylthio)-1,2,4-triazole* were isolated, m.p. 141—142°C. Since the m.p. of this compound was stated by Sandström[13] to be 148—148.6°C it was submitted to elemental analysis. (Found: C 27.47; H 4.70; N 31.75. Calc. for $C_4H_8N_4S_2$: C 27.25; H 4.58; N 31.79). The NMR spectrum (in dimethylsulfoxide-d_6) exhibited only one signal at $\tau = 7.47$ ppm, consistent with the assigned structure.

4-Dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-one (IX). At room temperature, (I) was dissolved in a tenfold excess of methyliodide. The following day the crystalline product produced was filtered off and dissolved in water. By washing twice with ether unreacted (I) was removed. The aqueous phase was then made basic with KOH and extracted twice with ether. After the combined ether extracts were dried with magnesium sulfate the solvent was removed in vacuum. Recrystallization of the residue from pentane furnished a colourless, crystalline product in 80 % yield, m.p. 90—91°C. (Found: N 30.00. Calc. for $C_6H_{12}N_4OS$: N 29.77). The NMR spectrum (in CCl_4) consisted of three singlets at $\tau = 7.63$ ppm (S—CH_3), $\tau = 7.10$ ppm (N(CH_3)$_2$, and $\tau = 6.69$ ppm (N—CH_3) with intensities in the proportions 1:2:1.

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