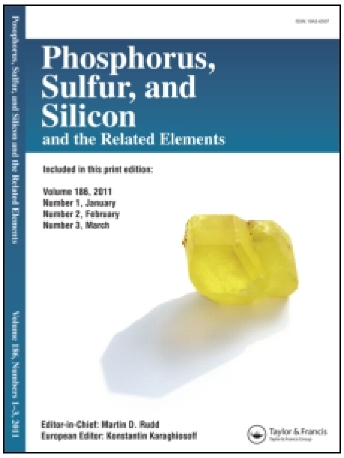

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THE S—S BOND IN N,N'-DITHIOBISAMINES. A RAMAN STUDY

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The Raman spectra of a series of N,N'-dithiobisamines, $(R_2N)_2S_2$ and their cyclic analogues compounds, 3,6-dialkyl-1,2,4,5,3,6-tetrathiadiazine have been studied in the 600–300 cm^{-1} region. Strong and polarized bands in the range 410–450 cm^{-1} were assigned to the stretching S—S vibration for the noncyclic NSSN compounds while that in the cyclic 3,6-dibenzyl-1,2,4,5,3,6-tetrathiadiazine this vibration appears in 480 cm^{-1}. The low ν(S—S) frequency values for N,N'-dithiobisamines are in agreement with their chemical behaviour. An approximately linear relationship between ν(S—S) and the S—S bond length, d(S—S) for N,N'-dithiobisamines and other disulfide compounds is proposed and discussed.

Key words: N,N'-dithiobisamines; raman spectra; disulfide compounds; S—S bond.

INTRODUCTION

Molecules having the sulfur—sulfur bond have been extensively studied due to their biological importance. The elucidation of the role and reactivity of the disulfide bond in biological systems has prompted several physical and chemical studies in smaller molecules containing this linkage.[1] The majority of these molecules contain the C—S—S—C moiety however less is known about compounds with the disulfide bond linked to other atoms than carbon, as N,N'-dithiobisamines[2,3] $R_2N—S—S—NR_2$. Although this class of compounds has been investigated as potential insecticides, fungicides, polymerization catalysts, corrosion inhibitors in lubricating oil and as stabilizers for polyurethane fibers,[4] their chemical, physical and spectroscopic properties have been only partially investigated.[4,5] The catalytic activity and other chemical features of these compounds are presumably related to the characteristics of the S—S as well as to the S—N bond. In this context and as a first step to future chemical studies of this type of compound, in this paper we report a Raman study of several N,N'-dithiobisamines and their cyclic analogue $C_6H_5—CH_2—N(S_4)N—CH_2—C_6H_5$. We previously have reported an IR study on these compounds.[4]

RESULTS AND DISCUSSION

The bands observed in the Raman spectra of a series of N,N'-dithiobisamines and the benzyl cyclic analogue 3,6-dibenzyl-1,2,4,5,3,6-tetrathiadiazine between 300–600 cm^{-1} are listed in Table I.

TABLE I

Raman spectra of $(R_2N)_2S_2$ between 300 and 600 cm^{-1}[a]

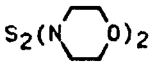
1a. $S_2[N(CH_3)_2]_2$[b]

1a
452 (10)(p)[c]
412 (9.5)(p)
390 (8.2)
345 (4.7)

1b. $S_2[N(CH_2CH_3)_2]_2$[b]

1b
438 (10)
390 (3)

1c.



Solid	Solution[d]
585 (3.8)	585 (7.5)(p)
450 (6.2)	450 (10)(p)
430 (10)	432 (10)
400 (2.9)	400 (3)(dp)
335 (4.7)	332 (4.2)(p)

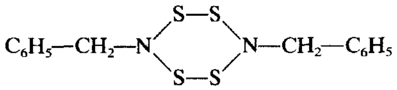
1d.

Solid	Solution
532 (4.1)	532 (4.6)(p)
445 (8.2)	444 (9.0)(p)
425 (10)	423 (10)(p)
340 (2.2)	338 (5)(p)

1e. $S_2[N(CH_2-C_6H_5)_2]_2$

Solid	Solution
590 (1.5)	450 (8.5)(p)
510 (1.4)	410 (10)(dp)
444 (7.3)	325 (6.2)(p)
420 (10)	
370 (4.1)	
336 (1.9)	

2.



Solid	Solution
572 (4.8)	576 (8.6)(p)
480 (10)	482 (9)(p)
460 (7.4)	466 (9.3)(p)
400 (6.9)	400 (10)(dp)
362 (6.9)	360 (1.7)(dp)
332 (2.7)	

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[a] Intersities in parenthesis (0 – 10).

[b] Liquid sample.

[c] p = polarized, dp = depolarized.

[d] Benzene solutions.

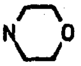
$R_2N-S-S-NR_2$

1

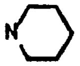
a $NR_2 = N(CH_3)_2$

b $NR_2 = N(CH_2CH_3)_3$

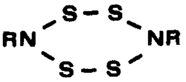
c $NR_2 =$



d $NR_2 =$



e $NR_2 = N(CH_2-C_6H_5)_2$



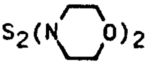
2

a $R = CH_2-C_6H_5$

b $R = C_6H_{11}$

TABLE II

ν(S—S) Stretching band for N,N'-dithiobisamine and $C_6H_5CH_2N(S_2)_2NCH_2C_6H_5$

	ν(S—S)
$S_2[N(CH_3)_2]_2$	452, 412
$S_2[N(CH_2CH_3)_2]_2$	438
	430, 450
	425, 445
$S_2[N(CH_2—C_6H_5)_2]_2$	420
$C_6H_5—CH_2N(S_2)_2N—CH_2C_6H_5$	480[a]

[a] We have previously assigned this band at 490 cm^{-1} on the basis of their IR band.

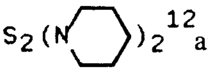
For compound 2b we were unable to obtain a good quality spectrum, owing to decomposition of the sample under the laser. The solid-phase Raman Spectra of polycrystalline samples **1c**–**1e** often have more one band in the ν(S—S) region (400–550 cm^{-1}). Similar behaviour was observed for solid disulfides compounds R—S—S—R.[6] To assign ν(S—S) bands unambiguously in this compound we rely on the solution-phase spectra (which are not complicated by the possible effects of crystal field) to reveal their inherent intensity. Our assignment were also supported by the polarization ratios measured in the solution Raman Spectra. Hence we assign the strongest and polarized band in the 300–600 cm^{-1} region to the S—S stretching vibration. Values are summarized in Table II. The strong Raman bands assigned to νS—S stretch are absent in the infrared counterpart as well as in the Raman spectra of their monothio-derivative analogues $R_2N—S—NR_2$.[7]

Compound **1c** and **1d** exhibit two intense and polarized bands between 400 and 500 cm^{-1}, which are present even in the solution-phase spectrum. Hence we believe that these two bands are associated with the S—S vibrations.

For compound **1a**, the neat liquid-phase Raman spectrum shows two S—S stretching bands at 412 and 452 cm^{-1} which can be due to the coexistence of the rotational isomers about the N—S bond in the liquid state. Similar behaviour has been found in liquid dialkyl disulfides.[8] For **1b** a broad band centered at 438 cm^{-1} probably involving the overlapping of two bands was observed.

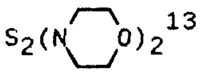
The Raman spectrum of compound **2** shows several bands in the S—S region. The band at 460 cm^{-1} is also present in the Raman and IR spectrum of N,N'-thiobisdibenzylamine[7] hence this band could not be attributed to the S—S bond. On the other hand, the band at 400 cm^{-1} is depolarized and it is also present in the Raman spectrum of N,N'-thiobisdibenzylamine. Then we assign tentatively the polarized band at 480 cm^{-1} as the ν(S—S). This value is in the range of ν(S—S) reported for other cyclic N—S—S—N compounds.[9,10]

The low ν(S—S) range found for N,N'-dithiobisamines 410–450 cm^{-1} is consistent with their weak S—S bond (D(S—S) = 30.8 Kcal/mol)[11] and with their long S—S bond (d(S—S) = 2.058 Å for



[12] and d(S-S)= 2.069

for



[13]

6

compared with the same linkage in dialkyl disulfides[6] where ν(S—S) fall in the region 500–550 cm^{-1} and *d*(S—S) are in the range 2.01–2.04 Å and D(S—S) = 60 Kcal/mol. Thus an approximately linear relationship between ν(S—S) and *d*(S—S) has been encountered for N,N′-dithiobisamines, dialkyl disulfides, H_2S_2,[14] and disulfur dihalides.[14–16] The plot is shown in Figure 1.[17]

The more weaker S—S bond in N,N′-dithiobisamines relative to the same linkage in another disulfide compound can be attributed to the stabilization of the thionitroxide radicals[11] by delocalization of the unpaired electron toward nitrogen atom.

$$R_2N—S—S—NR_2 \xrightarrow{\Delta} 2R_2N—S\cdot \leftrightarrow R_2\dot{N}{=}S \leftrightarrow R_2\overset{+}{N}—S^-$$

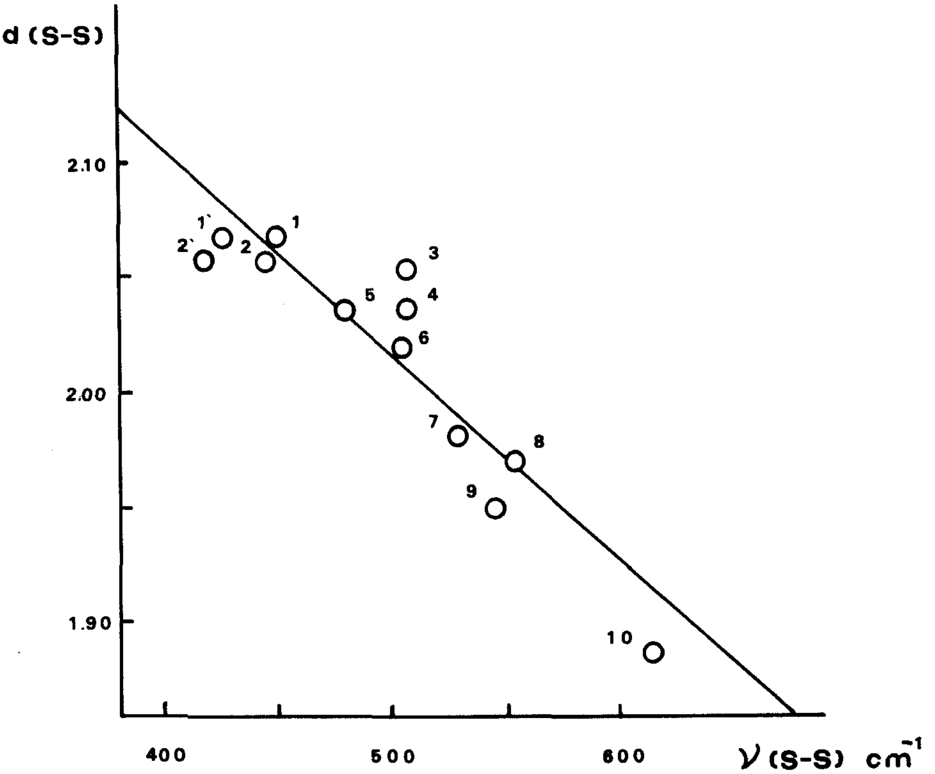


FIGURE 1 Correlation of the S—S distance *d*(S—S) vs the stretching S—S frequency νSS. Values were taken from References 6, 8 and 12–16. Numbers are: 1,1′) N,N′-dithiobis(morpholine), 2,2′) N,N′-dithiobis(piperidine), 3) hydrogen disulfide, 4) dimethyldisulfide, 5) 3,6-dibenzyl 1,2,4,5,3,6-tetrathiadiazine, 6) dibenzyldisulfide, 7) disulfur dibromide, 8) Trifluoromethylfluoride disulfide, 9) disulfur dichloride, 10) disulfur difluoride.

Similar arguments have been invoked to explain the low bond dissociation energy for RSSSSR compounds.[18]

The relationship shown in Figure 1 can be used to estimate the ν(S—S) band when the Raman spectrum is complicated and d(S—S) is known.

For example the compounds $MeSO_2$—CCl_2—S—S—CCl_2—SO_2Me although their Raman Spectrum is known, the assignment of their νS—S band is not straightforward.[19] Using the reported d(S—S) = 2.018 Å value for $(MeSO_2$—CCl_2—$S)_2$ a predicted value 515 cm^{-1} is obtained. Then the polarized bands at 542 and 491 cm^{-1} could be associated with the S—S stretching vibration.

EXPERIMENTAL

Dithiobisamines and cyclo-C_6H_5—$CH_2N(S_4)N$—CH_2—C_6H_5, C_6H_{11}—$N(S_4)N$—C_6H_{11} were prepared as reported previously.[4]

Raman Spectra were obtained on a Coderg Raman Spectrometer with Coherent-Radiation-Kryptonlaser Model 500 K (λ = 48800 pm). Depolarization measurements were made with a normal type polarization set. Polycrystalline powdered or pure liquid samples were used. Polarization data were obtained from benzene solution.

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REFERENCES

1. S. Oae, "Organic Chemistry of Sulfur." Plenum Press, Chap. 6, Plenum Press, New York (1977).
2. Q. E. Thompson, *Quart. Reports Sulfur Chem.*, **5**, 245 (1970).
3. D. R. Hogg, *Compr. Org. Chem.*, **3**, 311 (1979), (Engl).
4. C. Diaz V. and A. Arancibia, *Phosphorus, Sulfur, Silicon*, **44**, 1 (1989) and References therein cited.
5. C. Diaz, *Phosphorus, Sulfur, Silicon*, **48**, 141 (1990).
6. H. E. van Wart and H. A. Scheraga, *J. Phys. Chem.*, **80**, 1812 (1976).
7. C. Diaz, E. Clavijo and G. González, *Spectrochimica Acta*, **39A**, 537 (1983).
8. H. Sugeta, A. Go and T. Miyazawa, *Bull. Chem. Soc. Jpn.*, **46**, 3407 (1973).
9. C. Domingo and J. M. Orza, *Spectrochimica Acta.*, **34A**, 1033 (1978).
10. B. D. Stone and M. L. Nielsen, *J. Am. Chem. Soc.*, **81**, 3580 (1959).
11. W. C. Danen and D. D. Newkirk. *J. Am. Chem. Soc.*, **98**, 516 (1976).
12. R. Kivekas and T. Laitalainen, *Acta Chem. Scand.*, **41B**, 213 (1987).
13. S. C. Nyburg and F. H. Pickard, *J. Cryst. Mol. Struct.*, **3**, 343 (1973).
14. R. Steudel, *Angew. Chem. Internat. Ed.*, **14**, 655 (1975).
15. C. J. Marsden, R. D. Brown and P. D. Godfrey, *J. Chem. Soc. Chem. Comm.*, 399 (1979).
16. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds." John Wiley, 1986.
17. The relationship d_{SS} = 0.00092 νSS + 2.47 was obtained by a linear last-squares analysis of the points. The linear correlation coefficient was r = 0.92.
18. I. Kende, T. L. Pickering and A. V. Tobolsky. *J. Am. Chem. Soc.*, **87**, 5582 (1965).
19. J. S. Grossert, M. M. Bharadwaj, J. B. Faught and A. Terzis, *Can. J. Chem.*, **58**, 1106 (1980).