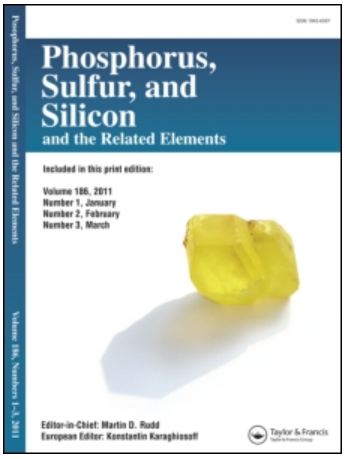


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SPECTROSCOPIC PROPERTIES OF *N,N'*-DITHIOBISAMINES AND THEIR CYCLIC ANALOGUES *N,N'*-DIALKYLCYCLOTETRASULFUR-1,4-DIIMIDES

C. Díaz[a]; A. Arancibia[a]
[a] Department of Chemistry, Faculty of Sciences, University of Chile, Santiago, Chile

To cite this Article Díaz, C. and Arancibia, A.(1989) 'SPECTROSCOPIC PROPERTIES OF *N,N'*-DITHIOBISAMINES AND THEIR CYCLIC ANALOGUES *N,N'*-DIALKYLCYCLOTETRASULFUR-1,4-DIIMIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 44: 1, 1 — 8
To link to this Article: DOI: 10.1080/10426508908043702
URL: http://dx.doi.org/10.1080/10426508908043702

Phosphorus, Sulfur, and Silicon, 1989, Vol. 44, pp. 1–8
Reprints available directly from the publisher
Photocopying permitted by license only

SPECTROSCOPIC PROPERTIES OF *N,N'*-DITHIOBISAMINES AND THEIR CYCLIC ANALOGUES *N,N'*-DIALKYLCYCLOTETRASULFUR-1,4-DIIMIDES

C. DÍAZ V. and A. ARANCIBIA†

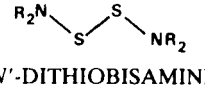
Department of Chemistry, Faculty of Sciences, University of Chile, Casilla 653 Santiago, Chile

(Received July 29, 1988)

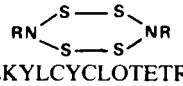
A series of *N,N'*-dithiobisamines $R_2N-S-S-NR_2$ $NR_2 = N(CH_3)_2$, $N(CH_2CH_3)_2$, N⟨⟩, N⟨⟩O, $N(CH_2—C_6H_5)_2$ and *N,N'*-dialkylcyclotetrasulfur-1,4-diimides $(RN)_2S_4$ R = CH_3, C_6H_{11}, $CH_2C_6H_5$ has been prepared and their ^{1}H-NMR, IR and UV spectra measured. The proton chemical shifts and the ν(S–N) frequency data are consistent with a chain open conformation for $R_2N-S-S-NR_2$ and with a cyclic structure for $(RN)_2S_4$. From UV spectral data, values of the disulfide dihedral angle were estimated and a structure for the $(RN)_2S_4$ compound proposed.

INTRODUCTION

Compounds containing the sulfur–sulfur bond have been extensively studied because the relation with biological problems. The S–S is an easily cleaved linkage which is an indispensable structural feature of most protein and polypeptides, and it is present in some smaller biomolecules. On the other hand some metal enzymes and metalloprotein contain the metal disulfide linkage.[1,2] Chemically the S–S bond is a functional group of diverse reactivity and interesting stereochemistry. However almost all the research on this matter has been made in substances involving the carbon–sulfur linkage and disulfilde compounds with other bond such as $R_2N-S-S-NR_2$[3] and their cyclic analogues $(RN)_2S_4$[4] have not received much attention. Our interest in the chemistry of S–N compounds[5–9] prompted us not to study this type of compounds.



N,N'-DITHIOBISAMINES



N,N'-DIALKYLCYCLOTETRASULFUR 1,4-DIIMIDAS

Although *N,N'*-dithiobisamines have been investigated as potential insecticides,[10] fungicides,[11] polymerization catalysts,[12] corrosion inhibitors in lubricating oil,[11] and as stabilizers for polyurethane fiber,[13] their chemical and spectroscopic properties have only been partially investigated.[3,11–16] 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. On the other hand

† Undergraduate Research Participant

$(RN)_2S_4$ are compounds that have received little attention and they have only been synthesized and poorly characterized.[4]

In this context and as a step previous to a future study of the coordinating properties of $(R_2N)_2S_2$ and $(RN)_2S_4$ in this paper we report a spectroscopic study of such compounds.

RESULTS AND DISCUSSION

IR and Raman spectra. The infrared spectra of $S_2(NR_2)_2$ and $S_4(NR)_2$ are described in Table I. The S–N bands for *N,N*-dithiobisamines were assigned with aid of a previous vibrational study of the related S–N molecules *N,N'*-thiobisamines $R_2N–S–NR_2$.[6,17] The assignments are shown in Table II. The spectra of the dithioderivatives are essentially similar to those of the monothioderivatives. As expected and as observed for other dithioderivatives,[18] the band corresponding to the S–S vibration is not observed. Nevertheless in the Raman spectra of *N,N*-dithiobis(dimethylamine) and dithiobis(diethylamine) presented in Table III, are observed intense bands at 450 cm^{-1} and 438 cm^{-1} attributable to the stretching S–S vibration. This ν(S–S) values are lower than those found in R–S–S–R compounds (500–550 cm^{-1})[18] and can be interpreted as a more weak S–S bond in dithiobisamines than dithioethers. This is also in agreement with the smaller S–S bond dissociation energy for dithiobisamines D(S–S) = 30.8 Kcal/mol[14] than D(S–S) = 60.70 Kcal/mol for dithioethers.[14]

The assignation for the S–N bond in the IR spectra of the dialkylcyclotetrasulfur diimides was made by comparison with vibrational data for other cyclic sulfur imides.[19,20] The values are displayed in Table II. Absorption below 600 cm^{-1} can be tentatively assigned to skeletal modes involving ν(S–S) stretching vibrations.

A decrease in the ν(S–N) is observed in going from the monothioderivates to the dithioderivates. This could be due to that the strained structure of the cyclic compounds preclude a good overlap between $d\pi$ (sulfur)–$p\pi$ (nitrogen) orbitals involved in the double bond character of the S–N linkage.[7,21] Thus in the *N,N*-thiobisamines the S–N bonds have some multiple character as indicated by the bond values 1.2–1.35,[6] whereas in the *N,N*-dithiobisamines the calculated bond order 1.04–1.19[22] indicates something closer to a single bond for the S–N linkage.

^{1}H-NMR spectra. The proton nuclear magnetic resonance data for the disulfide compounds are shown in Table IV. In general the proton signals are those of the $R_2N–S–NR_2$ compounds,[7] however the chemical shift values are different due to the distinct chemical environments. The resonance line of the α proton of the NR_2 groups moves toward to the high field on going from $R_2N–S–NR_2$ to $R_2N–S–S–NR_2$ indicating an increase of the shielding on those protons. This could be due to the decrease of the formal oxidation number of sulfur from 2^+ in the *N,N'*-thiobisamines to 1^+ in the dithiobisamines. In contrast a notable increase in the chemical shift values is observed on going from $R_2N–S–S–NR_2$ (or $R_2N–S–NR_2$) to the cyclic $(RN)_2S_4$ compounds. This can be interpreted as a decrease of the shielding of the respective α protons due to the larger electronegativity of the nitrogen atom in the cyclic structure (high N sp^2

TABLE I

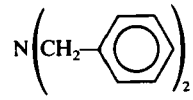
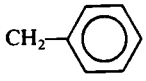
Infrared spectra of *N,N'*-dithiobisamines and *N,N'*-dialkylcyclotetrasulfur-1,4-diimidas (cm^{-1})

$S_2[N(CH_3)_2]_2$[a]	$S_2[N(CH_2CH_3)_2]_2$[a]	$S_2\left[N\text{—}\square\text{—}O\right]_2$[b]	$S_2\left[N\text{—}\square\text{—}O\right]_2$[b]	$S_2\left[N(CH_2\text{—}\bigcirc)_2\right]_2$[b]	$S_4(NCH_3)_2$[b]	$S_4\left(N\text{—}CH_2\text{—}\bigcirc\right)_2$[b]	$S_4(N\text{—}C_6H_{11})_2$[b]
2990 s[c]	2970 vs	2940 s	2978 m	3092 w	2980 w	3085 w	2960 s
2940 vs	2935 s	2920 s,sh	2920 w	3065 w	2955 m	3064 w	2930 vs
2870 s,sh	2900 m,sh	2862 m	2900 w	3038 w	2910 w	3035 w	2900 s
2860 s	2875 m,sh	2852 m	2865 m	2921 w	2870 w	2915 w	2860 s
2830 s	2840 m	2025 m	2846 m	2892 w	2850 w	2855 w	1449 m
2782 m	1465 m	2810 m,sh	1462 s	2840 m	2780 vw	1490 m	1346 w
1445 vs	1445 m	1461 m	1455 s	1493 m	1420 m	1450 m	1266 vw
1420 m	1327 s	1450 m,sh	1392 m	1452 s	1375 m,sh	1435 sh	1245 vw
1230 w	1360 m	1439 st	1350 m	1364 m	1255 s	1345 s	1042 s
1190 s	1335 m	1358 m	1300 w	1345 w	1115 s	1330 m	1035 w,sh
1134 m	1290 m	1291 m	1379 s	1320 w	1070 vs	1308 w	954 m
1089 vw	1180 s	1265 m	1354 s	1238 vw	795 s	1210 w	899 m
1032 m	1158 s	1216 vs	1200 w	1220 vw	700 s	1072 w	849 w
980 m,sh	1105 w	1151 m,sh	1108 vs	1205 vw	549 w	1008 s	752 m
950 s,sh	1080 m	1146 m	1054 m	1105 m	480 s	988 m	640 m
942 vs	1060 m	1100 s	938 s	1070 m	390 w	900 w	532 m
645 s	1030 m	1060 m	924 vs	1035 w		830 m	495 w
410 m	1020 m,sh	1032 s	908 s	1025 m		750 m	
	892 s	1025 m	843 s	969 w		727 vs	
	793 m	960 m	680 s	935 s		688 vs	
	640 s	919 vs	583 w	896 m		595 m	
	605 s	860 s	442 w	798 s		490 m	
	450 vw	834 s	400 w	786 vs		460 s	
		670 vs	392 w	695 s			
		531 m		687 s			
		434 s		670 w			
				605 w			
				495 w			
				455 w			

[a] Liquid, thin films, KBr plates.
[b] Solid, KBr disc.
[c] vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.

TABLE II

Assignments of ν(S–N) and ν(S–S) band in *N,N'*-dithiobisamines and *N,N'*-dialkylcyclotetrasulfur-1,4-diimidas

Compounds	ν(S–N) as	ν(S–N) sym.	ν(S–S)
$(R_2N)_2S_2$			
NR_2: $N(CH_3)_2$	942	645	450
$N(CH_2CH_3)_2$	892	640 605	438
	919	670	
	938	680	
	935	670	
$(RN)_2S_4$			
R: CH_3	795	700	
C_6H_{11}	752	640	495
	830	—	490

character) than the chain structure (close to sp^3 character of nitrogen). Consistent with this other cyclic S–N–R compounds[23] also exhibit higher proton chemical shift than their acyclic analogues.[7]

UV spectra. The UV-electronic spectral data for S–N compounds are presented in Table V. The longest wavelength transition in the spectra of the *N,N'*-dithiobisamines was assigned by comparison with a UV-spectral studies for dialkyldisulfides.[24–26] The absorption band observed at ca. 250 nm is assigned to a $n_a \rightarrow \sigma^*$SS transition in the Boyd's notation.[24] This assignment involving the disulfide chromophore is consistent with the fact that the respective monothioderivatives R_2N–S–NR_2 and its amine precursor does not absorb above 230 nm.[27,28]

TABLE III

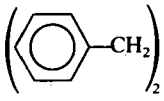
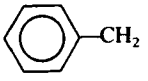
Raman spectra of $S_2(NR_2)_2$ in the range 1500–200 cm^{-1} [a]

$S_2[N(CH_3)_2]_2$	$S_2[N(CH_2CH_3)_2)_2$
1450 (1)[b]	1460 (1.3)
945 (1)	1060 (1.3)
648 (8.2)	650 (2.4)
452 (10)	640 (2.1)
412 (9.5)	620 (2.1)
390 (8.2)	438 (10)
345 (4.7)	390 (2.9)

[a] Liquid sample.
[b] Intensities in parenthesis (0–10).

TABLE IV

Proton magnetic resonance spectra of *N,N'*-dithiobisamines, *N,N'*-dialkylcyclotetrasulfur-1,4-diimides and its monothioderivatives

R_2N		δ(ppm from TMS)[a] $R_2N-S-S-NR_2$	$R_2N-S-NR_2$	Δ[b]
$[(CH_3)_2N$		2.53 (s)	2.96	0.43
$[(CH_3CH_2)_2N$	CH_3	1.16 (t)	1.16	0.0
	CH_2	2.71 (c)	3.03	0.32
	CH_2N	1.55 (m)	1.56	−0.02
	$(CH_2)_3$	2.80 (m)	3.23	0.43
	CH_2N	2.80 (m)	3.20	0.40
	CH_2O	3.70 (m)	3.60	−0.10
	CH_2	3.93 (s)	4.20	0.27
	C_6H_5	7.13 (m)	7.21	0.08
	$(RN)_2S_4$			
CH_3		3.36 (s)		
C_6H_{11}	CH	1.43 (m)		
	$(CH_2)_5$	2.31 (m)		
	CH_2	5.1 (s)		
	C_6H_5	7.2 (m)		

[a] CCl_4 solution, s = singlet, d = doublet, t = triplet, c = quartet, m = multiplet.

[b] $\Delta = \delta(R_2N)_2S - \delta(R_2N)_2S_2$.

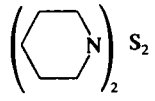
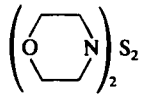
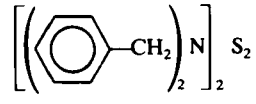
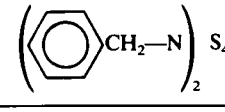
For the *N,N'*-dithiobis(dibenzylamine) derivate the corresponding $n_a \rightarrow \sigma^*SS$ transitions was not possible to assign because the very intense absorptions of the benzene group occurs in the same region.[29]

Analogously the absorption bands at 280–295 nm observed in the spectra of the *N,N'*-dialkylcyclotetrasulfur diimides, may be assigned to a $n_a \rightarrow \sigma^*SS$ transition.

Data of Table V indicate that the lowest absorption band of $R_2N-S-S-NR_2$ appears around 250 nm whereas the respective band for the cyclic $(RN)_2S_4$ compounds is observed around 290 nm. Several experimental[26,30] and theoretical studies[24,25] have discussed the relationship between the maximum of the longest wavelength ultraviolet disulfide absorption band and the CSSC dihedral angle for dialkyldisulfides. The results can be summarized by the linear relation shown in Figure 1. As the CSSC dihedral angle is opened from 0 to 90° the absorption maximum of the first UV band shifts from near 370 to about 250 nm. Also the extinction coefficient increases several fold with an increase of the dihedral angle.[24] Notwithstanding the fact that this correlation has been established from dialkyldisulfide compounds,[16,24,26,30] it seems likely that it also may be used with the *N,N'*-dithiobisamines. This approximation is valid because the similar shape

TABLE V

UV spectral data for $S_2(NR_2)_2$ and $S_4(NR)_2$ [a]

Compound	λ max (ε) for $n \rightarrow \sigma^*$SS transition
$[(CH_3)_2N]_2S_2$	251 (5000)
$[(CH_3CH_2)_2N]_2S_2$	259 (5432)
	256 (5754)
	251 (5128)
	b
$(CH_3—N)_2S_4$	280 (480)
$(C_6H_{11}N)_2S_4$	295 (375)
	294 (676)

[a] In cyclohexane solution, λ in nm.
[b] Hidden under the benzene ring transitions.

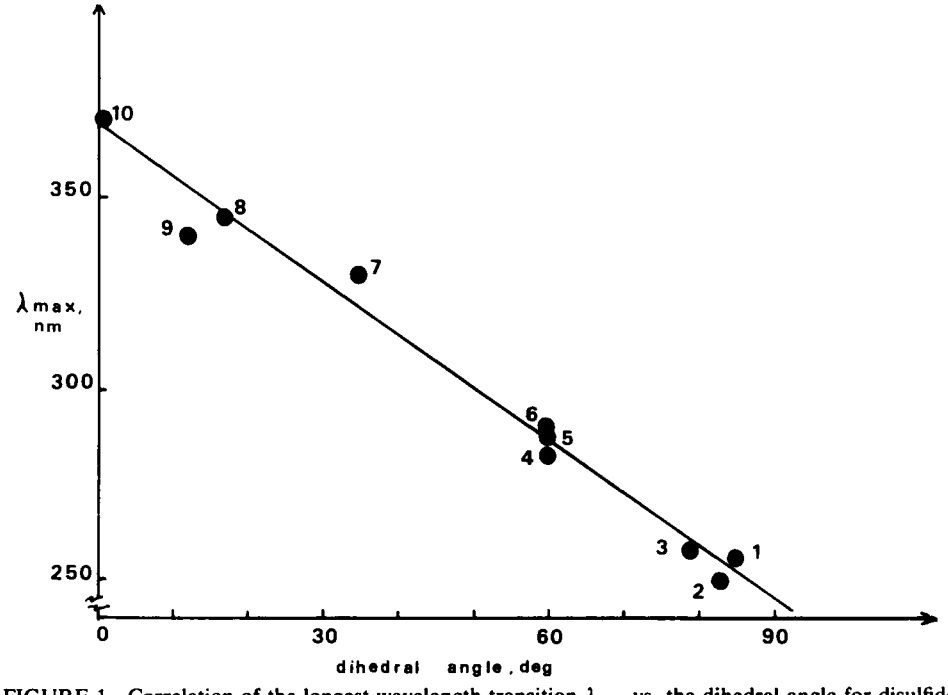


FIGURE 1 Correlation of the longest wavelength transition λ_{max} vs. the dihedral angle for disulfide compounds. Values were taken from references 16, 24, 26 and 30. Numbers are: 1) Dimethyl disulfide; 2) Diethyl disulfide; 3) 1,2-Dithiepane; 4) 4,5-Dihidroxy-1,2-dithiane; 5) 1,2-Dithiane; 6) trans 2,3-Dithiadecalin; 7) 1,2-Dithiolane; 8) Acetylaranotin; 9) Gliotoxin; 10) 1α, 5α-Epidithioandrostane-3α, 17β-diol.

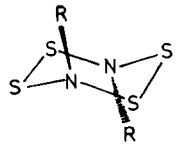


FIGURE 2 Structure proposed for $S_4(NR)_2$ compounds.

of the HOMO of $R_2N-S-S-NR_2$[31] and $R-S-S-R$[24] as well as because the similar dependence of the S–S dihedral angle.[31,24] For $R_2N-S-S-NR_2$ and R–S–S–R the most stable conformation occurs at ca. 90° as showed theoretical calculations.[31,24] Using the Figure 1 we have obtained values of the S–S dihedral angle for *N,N'*-dithiobisamines and for their cyclic analogues. For $R_2N-S-S-NR_2$ the values are in the range 84–86° while that for $(RN)_2S_4$ a value around 60° was estimated. The dihedral angles obtained for *N,N'*-dithiobisamines are in good agreement with those determined from a X-ray structure study for the dithiobis(morpholine). For this, the value is 84.2°[32] whereas the calculated is 86°. This also is in accord with the structure in solution suggested by proton NMR data.[15]

For the $(RN)_2S_4$ compounds the cyclic constitution has only been suggested in basis of molecular weight measurement[4] and not structural determination have been made. The value of the S–S dihedral angle of 60° estimated for us for these compounds is consistent with the cyclic structure shown in the Figure 2. This also is in agreement with the IR and ^{1}H-NMR data above discussed.

EXPERIMENTAL

Infrared, Raman, proton NMR and UV-visible spectral data were obtained as described elsewhere.[5,9] Commercial S_2Cl_2 (Fluka) was purified by distillation over sulfur and the fraction boiling between 136–138°C collected and immediately used. Amines were dried by reflux with KOH before use. For high boiling point amines distillation under reduced pressure was used.

Petroleum ether and diethylether were purified by reflux over sodium and distillation.

The method used for the preparation of the sulfur compounds were essentially those reported in the literature[3,4] with some modifications.

N,N'-dithiobisamines. A 1000 ml three necked flask equipped with a mechanical stirrer, a reflux condenser with a drying tube, and a pressure-equilibrated dropping funnel was charged with 0.71 moles of the respective amine in 500 ml of petroleum ether at 0°C. With dimethylamine a saturated solution was used. For the synthesis of *N,N'*-dithiobis(dibenzylamine) a mixture of 0.15 moles of dibenzylamine and 0.15 moles of triethylamine was used. To this 0.17 moles of S_2Cl_2 in 100 ml of solvent was added dropwise over a period of 1 h. After the addition of S_2Cl_2 the reaction mixture was allowed to warm at room temperature and the solid filtered. The solvent was removed in vacuo and the crude product recrystallized from ethanol. The liquid diethyl and dimethyl-derivatives were purified by fractional vacuum distillation. Physical properties were similar with that reported in literature.[3] All sulfur compounds were stored in the freezer.

N,N'-dialkylcyclotetrasulfur 1,4-diimides. These compounds were obtained by reaction of S_2Cl_2 and the respective primary amine using a high dilution and adding the reactant simultaneously. A 2000 ml three-necked flask equipped with a mechanical stirrer was charged with 800 ml of diethylether at 0°C. To this 0.05 moles of the respective primary amine and 0.15 moles of S_2Cl_2 in two separate dropping funnel with drying tubes, were added dropwise at the same time over a period of 90 min. Upon complete addition of S_2Cl_2 and the amine, the reaction was allowed to continue with stirring at ambient temperature for an additional 30 min. Following this the precipitate was filtrate off and the filtrate was concentrate to 50–100 ml. Then the solution placed in the freezer overnight. Filtration of the resulting crystals afforded the pure products. In the case of the methylamine derivative the ethereal solution was concentrated and then 10 ml of diethyl ether at −80°C was added. The solvent then was quickly evaporated under reduced pressure until ca. fourth of the initial volume. The

solution was placed in a cold bath (−80°C) and the resulting crystals filtered through a cold frit and dried in vacuum. The compounds are white solid and also were stored in the freezer. Physical properties were similar with that reported.[4]

ACKNOWLEDGEMENTS

We thank the Dirección Técnica de Investigación D.T.I. of University of Chile for financial support of this work. In addition we are grateful to Dr. E. Clavijo for the Raman Spectra measurement.

REFERENCES AND NOTES

1. L. G. Warner, T. Ottersen and K. Seff, *Inorg. Chem.* **13,** 2819 (1974) and references therein cited.
2. H. C. Freeman *et al.*, *Nature* **272,** 319 (1978).
3. Q. E. Thompson, *Quart. Reports Sulfur Chem.* **5,** 245 (1970).
4. M. Becke-Goehring and H. Jenne, *Chem. Ber.* **92,** 1149 (1959).
5. G. González, C. Díaz and S. Copaja, *Monatsh. Chem.* **114,** 177 (1983).
6. C. Díaz, E. Clavijo and G. González, *Spectrochim. Acta* **39A,** 537 (1983).
7. C. Díaz, S. Copaja and G. González, *Phosphorus and Sulfur* **22,** 317 (1985).
8. C. Díaz and G. González, *Inorg. Chim. Acta* **85,** 61 (1984).
9. C. Díaz. *Polyhedron* **4,** 1269 (1985).
10. W. D. Stewart and J. H. Standen, U.S. Patent 2,501, 191 (March 21, 1950); *Chem. Abstr.* **44,** 6570 (1970).
11. D. H. Clemens, U.S. Patent 3,394, 185 (July 23, 1968); *Chem. Abstr.* **69,** 95953z (1969).
12. K. Machida, H. Ikegami and K. Hisamura, Japanese Patent 6,921, 101 (Sept. 9, 1969); *Chem. Abstr.* **72,** 13204f (1970).
13. I. Suzuki, K. Ichikawa, K. Murayama and S. Morimura, German Patent 1,928, 915 (Dec. 11, 1969); *Chem. Abstr.* **72,** 4481k (1970).
14. W. C. Danen and D. D. Newkirk, *J. Am. Chem. Soc.* **98,** 516 (1976).
15. V. W. Hu, J. W. Gilje and T. T. Bopp, *Inorg. Chem.* **12,** 955 (1973).
16. S. Oae, "Organic Chemistry of Sulfur", Plenum Press, New York (1977).
17. C. Díaz, *Acta Sud. Am. Quím.* **3,** 15 (1983).
18. H. E. Van Wart and H. A. Sheraga, *J. Phys. Chem.* **80,** 1812 (1976).
19. J. Nelson, *Spectrochim. Acta* **27A,** 1105 (1971).
20. C. Domingo and J. M. Orza, *Spectrochim, Acta* **34A,** 1033 (1978).
21. A. J. Banister, F. F. Moore and J. S. Padley, *Spectrochim. Acta* **23A,** 2705 (1967).
22. These values were calculated using the relationships 2 and 4 of reference 6.
23. B. A. Olsen and F. P. Olsen, *Inorg. Chem.* **8,** 1736 (1969).
24. D. B. Boyd, *J. Am. Chem. Soc.* **94,** 8799 (1972).
25. D. B. Boyd, *J. Phys, Chem.* **78,** 1554 (1974).
26. B. Panijpani, *J. Chem. Educ.* **54,** 670 (1977) and references therein.
27. F. Feher and H. Munzer, Chem. Ber. **96,** 1131 (1963).
28. H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", Wiley, New York (1962).
29. For Dibenzylamine absorption are observed below 260 nm.
30. L. A. Neubert and M. Carmack, *J. Am. Chem. Soc.* **96,** 943 (1974).
31. H. Bock, W. Schulz and U. Stein, *Chem. Ber.* **114,** 2632 (1981).
32. S. C. Nyburg and F. H. Pickard, *J. Cryst. Mol. Struct.* **3,** 343 (1973).