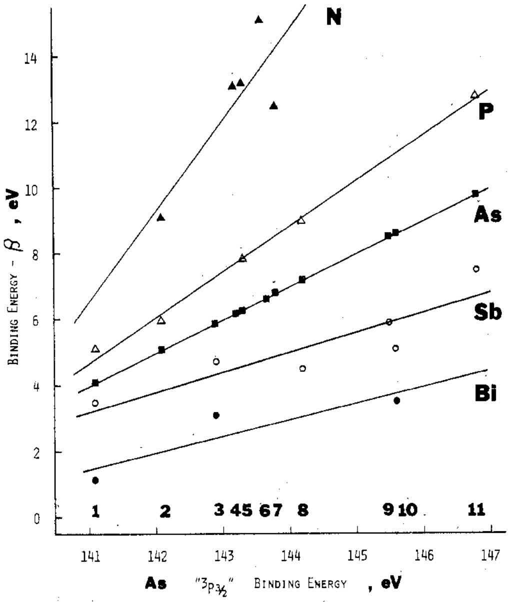

Figure 2. The nitrogen "1s" ($\beta = 389$), phosphorus "2p" ($\beta = 125$), arsenic "$3p_{3/2}$" ($\beta = 137$), antimony "$3d_{5/2}$" ($\beta = 525$), and bismuth "$4f_{7/2}$" ($\beta = 156$) corrected binding energies *vs.* the arsenic "$3p_{3/2}$" binding energies. The relative shifts for the compounds of group Va are as follows: N, 1.00; P, 0.50; As, 0.36; Sb, 0.21; Bi, 0.18. The numbers near the bottom of this figure indicate the position of the binding energies of those compounds having the same number, kind, and arrangement of substituent atoms in the following arsenic compounds: 1, As; 2, $(C_6H_5)_3As$; 3, As_2S_3; 4, As_4N_4; 5, $(C_6H_5)_3AsO$; 6, $NaAsO_2$; 7, $(C_6H_5)_4AsCl$; 8, As_2S_5; 9, As_2O_5; 10, As_2O_3; 11, $KAsF_6$.

model[12] (*i.e.*, $\Delta E \propto 1/r$), was found once again. However, the overall-shift ranges for the group Va elements were significantly lower than those found for the corresponding group IVa elements[2] with the same charge on the ions. It should be noted that the relative shifts with respect to nitrogen in this work are much larger than those previously reported.[1] The difference resulted from what would appear to be an unequal perturbation of the valence electrons upon forming an outer-electron configuration by using d orbitals[1] in a first-row atom such as nitrogen (two separable ranges are actually observed[1] for nitrogen, one with d's and one without d's).

The experimentally measured binding energies for the N "1s", P "2p", As "$3p_{3/2}$", Sb "$3d_{5/2}$", and Bi "$4f_{7/2}$" electrons are plotted against the arsenic "$3p_{3/2}$" binding energies of compounds containing equivalent substituents on the group Va element (Figure 2). Unfortunately, only a small number of related nitrogen compounds[13] which were referenced only with respect to the residual C "1s" line[14] (some of these compounds were not identical with the corresponding arsenic compounds) were available for comparison purposes. However, the results certainly demonstrate general chemical shift effects similar to those observed for the group IVa compounds.[2] The nitrogen-containing compounds exhibit the largest shift effects of group Va and decreasing effects are seen with increasing atomic size. The relative shifts of the group Va compounds are as follows: N, 1.00; P, 0.50; As, 0.36; Sb, 0.21; and Bi, 0.18; they are quite similar to those reported for the group IVa compounds[2] as expected from a comparison of the atomic SCF calculations and the simple atomic radii ratios[2] of the two groups of elements. The considerably smaller experimental values of the relative shifts of As, Sb, and Bi as compared to their free-atom values may possibly be attributed to more $p_\pi \rightarrow d_\pi$ feedback in the compounds of these elements as compared to similar phosphorus compounds.

Registry No. $KSbF_6$, 16893-92-8; $SbCl_5[(C_6H_5)_3PO]$, 18828-04-1; $(C_6H_5)_4PSbCl_6$, 38188-09-9; SbF_3, 7783-56-4; $K_2H_2Sb_2O_7 \cdot 4H_2O$, 10090-54-7; Sb_2O_5, 1314-60-9; $Sb(OCOCH_3)_3$, 6923-52-0; Sb_2O_3, 1309-64-4; SbI_3, 7790-44-5; $Sb(SC_{12}H_{25})_3$, 6939-83-9; $NaSbO_3$, 15432-85-6; Sb_2S_3, 1345-04-6; Sb_2S_5, 1315-04-4; AlSb, 25152-52-7; Sb, 7440-36-0; BiF_3, 7787-61-3; $Bi(SO_4)_3 \cdot H_2O$, 38162-92-4; BiOCl, 7787-59-9; $Bi_2Ti_2O_7$, 12048-51-0; $(BiO)_2Cr_2O_7$, 37-235-828; BiI_3, 7787-64-6; Bi_2O_3, 1304-76-3; $Bi_2O_4 \cdot 2H_2O$, 12-233-293; $NaBiO_3$, 12232-99-4; Bi_2S_3, 1345-07-9; Bi, 7440-69-9.

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[12] J. M. Hollander and D. A. Shirley, *Ann. Rev. Nucl. Sci.*, **20**, 435 (1970).

[13] R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1968).

[14] B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **1**, 286 (1970).

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Stereochemistry of the Bis(amino)sulfides and -disulfides

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Although the stereochemistry of sulfur-nitrogen compounds has aroused much recent interest,[1-3] little is known of the conformation of species containing several S-N bonds or of the dynamics of the stereochemical processes occurring in such molecules. This note reports the results of a dynamic nmr investigation of several bis(amino)sulfides, $(R_2N)_2S_n$, where R = CH_3, C_2H_5, or i-C_3H_7 and n = 1 or 2. These compounds represent a series whose behavior should reflect properties of simple sulfur-nitrogen frameworks containing two S-N bonds. In addition the disulfides are of interest because there is no information presently available on the stereochemical relationships within an N-S-S-N unit even though the S-S moiety is of considerable chemical and biological interest.

Experimental Section

The compounds $(R_2N)_2S_n$ (R = CH_3, C_2H_5, C_3H_7; n = 1, 2) were prepared *via* the direct reaction of S_nCl_2 with the appropriate amine using a literature method.[4] Nmr spectra were recorded in CCl_2F_2 solutions on an HA-100 spectrometer equipped with variable-

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[1] M. Raban and T. Cho, *Int. J. Sulfur Chem., Part A*, **1**, 269 (1971), and references therein.

[2] W. B. Jennings and R. Spratt, *Chem. Commun.*, 1418 (1970).

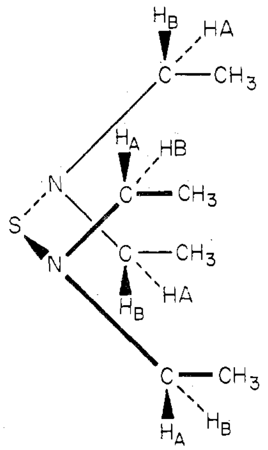
[3] H. J. Jakobsen and A. Senning, *Chem. Commun.*, 617 (1967).

[4] (a) M. Michaelis, *Chem. Ber.*, **28**, 165, 1013 (1895); (b) F. Lengfeld and J. Stieglitz, *ibid.*, **28**, 575 (1895); (c) E. S. Blake, *J. Amer. Chem. Soc.*, **65**, 1267 (1943); (d) A. B. Burg and H. W. Woodrow, *ibid.*, **76**, 219 (1954).

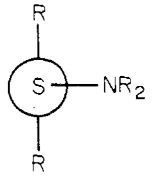
temperature probe and a spin decoupler. Rate constants at the coalescence temperature, T_c, for the interconversion of conformers were estimated using the expression $K_c = \pi/\sqrt{2}\,(\Delta\nu^2 + 6J_{AB}^2)^{1/2}$ or $k_c = \pi/\sqrt{2}\Delta\nu$, as appropriate, and free energies of activation at coalescence, $\Delta G_c^{\ddagger}$, obtained using these rate constants and the Eyring equation. Nmr parameters and results are summarized in Table I and Figures 1 and 2.

Discussion

Although the alkyl groups in the three bis(amino)sulfides, $(R_2N)_2S$, remain equivalent at least to −120°, the spectra of two of them are temperature dependent since the methylene protons in $[(C_2H_5)_2N]_2S$ and the methyl groups in the diisopropylamino derivative become nonequivalent at low temperature. (A 13-Hz geminal coupling constant in the diethylamino compound demonstrates the diastereotopic groups are attached to the same carbon atom.) The stereochemical exchanges, the slowing of which could give rise to this temperature dependency, are either nitrogen inversion or S-N bond rotation. The latter, however, can be assigned as the rate-limiting process since (1) S-N torsion has been shown to give rise to barriers of a similar magnitude in other S-N compounds while nitrogen inversional barriers in these compounds are either very low or the nitrogen is, in fact, planar,[1-3,5] and (2) the barriers observed in the bis(amino)sulfides increase with increasing steric bulk on the nitrogen as would be expected for a hindered rotation where steric crowding occurs in the transition state. Given this assignment the low-temperature spectra indicate a conformation in which R groups bonded to a planar (or rapidly inverting) nitrogen remain equivalent as S-N rotation slows. The only reasonable configuration which satisfies this criterion is one in which the two NR_2 planes are perpendicular to the SN_2 plane (structure I). Considering $[(C_2H_5)_2N]_2S$ it is clear that methylene protons should become diastereotopic as this process slows, as would the methyl groups in the analogous isopropyl derivative. A Newman projection down one S-N bond



I



more clearly shows the relative orientations of the various substituents. From this view it is clear that the stereochemistry about each of these bonds closely resembles that in other S(II)-N compounds.[6-8]

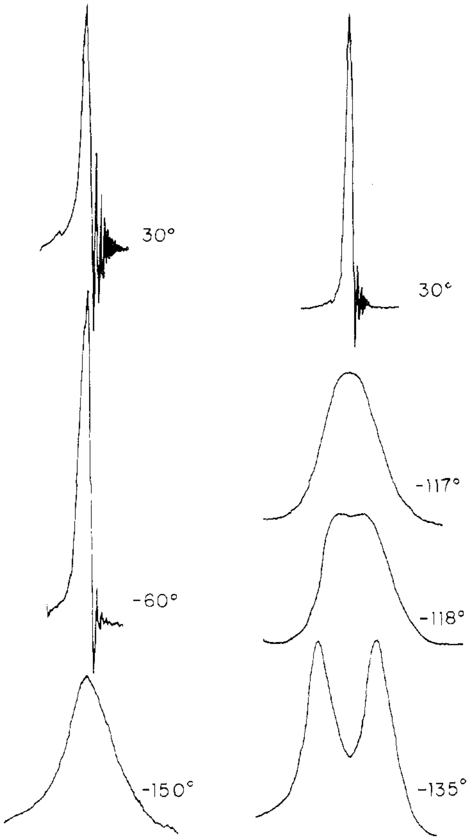


Figure 1. Variable-temperature ^1H nmr spectra of $[(CH_3)_2N]_2S$ (left) and $[(CH_3)_2N]_2S_2$ (right).

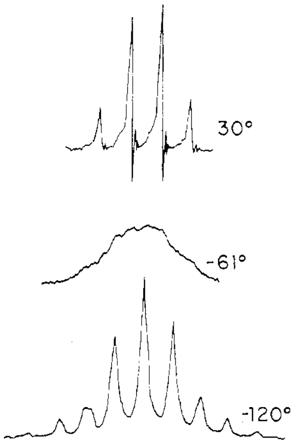


Figure 2. Methylene portion of the ^1H nmr spectrum of $[(C_2H_5)_2N]_2S$.

The bis(amino)disulfides are more complex. If rapid rotation were to occur about the S-S and S-N bonds and if N inversion was rapid, all alkyl groups would be equivalent. In $[(CH_3)_2N]_2S_2$ and $[(C_3H_7)_2N]_2S_2$ at 30° all groups do appear to be equivalent. In fact, however, it is likely that the R groups actually reside in different sites between which the chemical shift differences are too small to allow their

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(5) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, 9, 401 (1970).

(6) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, 91, 6677 (1969).

(7) R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, *J. Amer. Chem. Soc.*, 93, 924 (1971).

(8) J. Kay, M. Glick, and M. Raban, *J. Amer. Chem. Soc.*, 93, 5224 (1971).

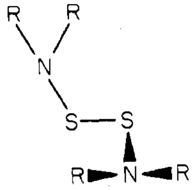
Table I. Nmr Data

Compd	Temp, °C	Type of spectrum	Chem shifts,[a] ppm (from TMS)	Coupling const,[a] Hz	T_c, °C	$\Delta\nu$, Hz	$\Delta G_c^{\ddagger}$, kcal/mol
$S[N(CH_3)_2]_2$	30	A_3	−2.97 (A)				
	−150	A_3	−3.06 (A)				
$S[N(C_2H_5)_2]_2$	30	A_2X_3	−3.07 (A)	7.0 (AX)			
			−1.12 (X)		−61	14.9	10.3
	−120	ABX_3	−2.43 (A), −2.68 (B)	13.0 (AB)			
			−1.12 (X)	7.0 (AX)			
$S[N(C_3H_7)_2]_2$	30	AX_6	−3.49 (A)	6.7 (AX)			
			−1.12 (X)		−61	3.1	11.4
	−80	AX_3Y_3	−3.49 (A)	6.6 (AX)			
			−1.10 (X), −1.12 (Y)	6.8 (AY)			
$S_2[N(CH_3)_2]_2$	30	A_3	−2.56 (A)		−118	5.8	8.1
	−130	A_3B_3	−2.53 (A), −2.58 (B)				
$S_2[N(C_2H_5)_2]_2$	30	$A_2X_3 + C_2Y_3$	−2.75 (A), −2.76 (C)	7.07 (AX)			
			−1.12 (X and Y)	7.11 (CY)	−70	20.5	10.0
	−120	$ABX_3 + CDY_3$	−2.63 (A), −2.74 (B)	7.16 (AX), 7.0 (BX)			
			−2.65 (C), −2.77 (D)	12.5 (AB)			
			−1.12 (X and Y)	6.8 (CY), 7.3 (DY)			
				12.5 (CD)			
$S_2[N(C_3H_7)_2]_2$	30	AX_6	−3.42 (A)	6.6 (AX)			
			−1.17 (X)				
	−110	AX_3Y_3	−3.42 (A)	6.7 (AX)	−82	2.3	10.4
			−1.16 (X), 1.18 (Y)	6.6 (AY)			

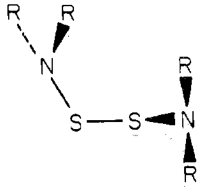
[a] The assignments of coupling constants and chemical shifts were confirmed by double-resonance experiments.

resolution by nmr because in the ambient temperature spectrum of $[(C_2H_5)_2N]_2S_2$ two distinct methylene quartets (separated by less than 1 Hz) are observed. This clearly indicates that in the diethyl derivative and probably in the other two disulfides as well that (since rapid nitrogen inversion would be expected at 30°) either S-N or S-S rotation must already be slow at room temperature.[9] Below 30° the spectra of all these disulfides are temperature dependent, the rate-limiting process being assigned to torsion about a bond rather than nitrogen inversion using arguments similar to those presented above for the bis(amino)sulfides. While it is not possible to determine unambiguously which rotation was observed to slow below ambient temperature and which had already slowed by 30° it is known that in diethoxy disulfide S-S rotation does not become rapid on the nmr time scale until considerably above room temperature.[10] Since the N-S barriers reported above for the bis(amino)sulfides and elsewhere for other S-N barriers[1-3] are near those measured for the exchanges observed below room temperature in $(R_2N)_2S_2$, we tentatively assign the barriers reported in Table I to N-S torsion.

The low-temperature spectrum of $[(C_2H_5)_2N]_2S_2$, which at −120° has become overlapping ABX_3 and CDY_3 spectra, shows not only that the ethyl groups occupy two different sites after N-S and S-S rotation have ceased (but while N inversion is still rapid) but also that the methylene protons on each are diastereotopic. (The low-temperature spectra of the other two disulfides can be interpreted similarly.) The observation of two equally populated alkyl group sites, combined with the nonequivalences of the methylene protons, make a planar N-S-S-N framework unlikely since reasonable structures would either have more or less than two R group sites or the methylene protons would not be diastereotopic. If, on the other hand, the structure is similar to other disulfides[10,11] and is nonplanar, the data can be explained by either of two logical structures



II



III

In II the R_2N planes contain the S-S bond axis while in III this plane is perpendicular to the NSS plane. While no discrimination can be made between these structures on the basis of our data, III may be the more reasonable since the conformation about the S-N bond in it is identical with that in I.

Registry No. $S[N(CH_3)_2]_2$, 2129-20-6; $S_2[N(CH_3)_2]_2$, 928-05-2; $S[N(C_2H_5)_2]_2$, 3768-61-4; $S_2[N(C_2H_5)_2]_2$, 15575-30-1; $S[N(C_3H_7)_2]_2$, 34066-25-6; $S_2[N(C_3H_7)_2]_2$, 38126-23-7.

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[9] Unfortunately $[(C_2H_5)_2N]_2S_2$ decomposes upon heating and we were unable to obtain spectra in the fast-exchange region.

[10] F. Seel, W. Gombler, and R. Budenz, *Justus Liebigs Ann. Chem.*, 735, 1 (1970).

[11] R. B. Fraser, G. Boussard, J. K. Saunders, J. B. Lambert, and C. E. Mixan, *J. Amer. Chem. Soc.*, 93, 3822 (1971).

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Disproportionation of Dithionate

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Aqueous dithionate is known to disproportionate in a slow acid-catalyzed reaction at high temperatures[1]