

# Structural Studies on the Sulfur—Nitrogen Bond. I.

## The Crystal Structure of Bis(morpholino)sulfide

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The structure of the title compound,  $[\text{O}(\text{CH}_2\text{CH}_2)_2\text{N}]_2\text{S}$ , has been determined by X-ray crystallographic methods. Fullmatrix least-squares refinement led to a conventional *R*-value of 0.050 for 2373 reflections.

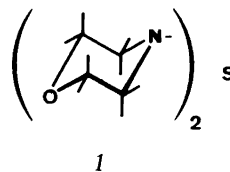
The crystals are monoclinic, space group  $P2_1/c$ . There are two fairly similar molecules per asymmetric unit. Cell dimensions (at  $-150^\circ\text{C}$ ) are:  $a = 11.207(2)$  Å;  $b = 15.658(3)$  Å;  $c = 11.574(2)$  Å;  $\beta = 90.19(2)^\circ$ . The molecule possesses a pseudo two-fold axis with the morpholino rings in the chair conformation and linked equatorially to the central sulfur atom. The NSN bond angle is  $113.2^\circ$  and the average S—N bond length is 1.680 Å. The sum of the bond angles at the nitrogen atoms is close to  $350.0^\circ$  and the direction of the nitrogen lone pairs is cisoidal to the sulfur lone pairs. The two morpholino groups of a molecule are slightly twisted; the torsion angles NSNC being about  $-67$  and  $+74^\circ$  for each morpholino ring.

Although being known for close to a century,<sup>1</sup> bis(dialkylamino)sulfides,  $(\text{R}_2\text{N})_2\text{S}$ , is a class of compounds which has only been the subject of limited studies. Their simple preparation was described by Blake<sup>2</sup> some 40 years ago and the compounds are known to be most stable toward both hydrolysis and thermal degradation. With the exception of  $(\text{Et}_2\text{N})_2\text{S}$ , bis(dialkylamino)sulfides are generally crystalline and colourless materials at room temperature.<sup>3</sup>

Bis(dialkylamino)sulfides are apparently quite unreactive species and only very powerful electrophilic species seem to be attacked by this class of compounds. Strongly alkylating agents such as  $\text{R}_3\text{O}^+$ -salts form *S*-alkylsulfonium salts<sup>4–6</sup> while the hard Lewis acid  $\text{BF}_3$  forms a fairly stable 1:2

adduct with  $(\text{Me}_2\text{N})_2\text{S}$  through N—B bonds.<sup>7</sup> Bis(dialkylamino)sulfides are thus in principle ambident but very weakly nucleophilic species;<sup>8</sup> the potential ambident nature but not the limited reactivity resembles that of  $(\text{R}_2\text{N})_3\text{P}$  and  $(\text{R}_2\text{N})_3\text{As}$ .<sup>9,10</sup> Contrary to the latter compounds  $(\text{R}_2\text{N})_2\text{S}$  exhibits none or only weak reactivity toward protic species and alcohols are convenient crystallization agents.

In order to improve our knowledge of the chemistry of  $(\text{R}_2\text{N})_2\text{S}$  it appears necessary to obtain more information with regard to both the electronic distribution within the N—S—N part of the molecules and also to the preferred conformation. The various studies published so far including mass



spectral studies,<sup>11,12</sup> NMR studies<sup>13,14</sup> and UV studies,<sup>15</sup> do not allow any definite conclusions to be made. X-Ray crystallographic examination appears to be a useful approach and in the present study we want to report on the crystal structure of bis(morpholino)sulfide,  $\text{Mor}_2\text{S}$  (*1*). By choosing morpholino groups as substituents, a nicely crystalline material was obtained and a comparison with the structure of  $(\text{MorS}-)_2$ ,<sup>16</sup>  $(\text{MorS}_2-)_2$ ,<sup>17</sup>  $\text{Mor}_3\text{P}$ <sup>9</sup> and  $\text{Mor}_3\text{As}$ <sup>10</sup> could be made. X-Ray studies of  $\text{S}_7\text{NSNMe}_2$  and of  $((\text{C}_6\text{H}_{11})_2\text{N})_2\text{S}$ <sup>18</sup> and an electron diffraction study of  $(\text{Me}_2\text{N})_2\text{S}$ <sup>19</sup> have recently been published.

## EXPERIMENTAL

**Material.** Bis(morpholino)sulfide,  $\text{Mor}_2\text{S}$ , was made as described in Ref. 2 from sulfur dichloride,  $\text{SCl}_2$ , freshly distilled from 2% phosphorus trichloride,  $\text{PCl}_3$ , to remove traces of  $\text{S}_2\text{Cl}_2$ .<sup>20</sup> The compound was first purified by sublimation; subsequent crystallization from ethanol yielded crystals suitable for the X-ray experiments. M.p. 124–125 °C (125 °C<sup>2</sup>); NMR ( $\text{CH}_2\text{Cl}_2$ ): [ $\delta$  3.23–3.37 (m, 8,  $\text{NCH}_2$ ), 3.56–3.70 (m, 8,  $\text{OCH}_2$ )]; IR (KBr-disc): 685  $\text{cm}^{-1}$  (S–N).

**X-Ray data.** Data for the measurements of cell dimensions and intensity data were collected on a SYNTEX P1 diffractometer using graphite crystal monochromated  $\text{MoK}\alpha$  radiation ( $\lambda=0.71069$  Å). The temperature at the crystal site was –150 °C, crystal size 0.1 × 0.4 × 0.4 mm. Cell parameters were determined by a least squares fit to the diffractometer settings of 15 general reflections with  $2\theta > 35^\circ$ . Intensities were measured with the  $\theta$ - $2\theta$  scan technique, scan speed 2–4°  $\text{min}^{-1}$  depending on the peak intensity, scan width  $\pm 1.0^\circ$  up to a  $\sin \theta/\lambda$  value of 0.60 Å<sup>-1</sup>. Background counts were taken for 0.35 times the scan time at each of the scan limits. Out of the 3618 unique reflections recorded, 2373 with  $I > 2.5\sigma(I)$  were retained for the structure analysis. The standard deviations for the intensities were calculated as  $\sigma(I) = [C_T + (0.02 C_N)^2]^{1/2}$ , where  $C_T$  is the total number of counts and  $C_N$  is the scan count minus background count. The intensities were corrected for Lorentz and polarization effects but not for absorption.

A description of the computer programs used for the structure determination is given in Ref. 21. Atomic form factors were those of Doyle and Turner<sup>22</sup> for the heavy atoms and of Stewart, Davidson and Simpson<sup>23</sup> for the hydrogen atoms.

## CRYSTAL DATA

Bis(morpholino)sulfide,  $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ , m.p. 124–125 °C. Monoclinic,  $a = 11.207(2)$  Å;  $b = 15.658(3)$  Å;  $c = 11.574(2)$  Å;  $\beta = 90.19(2)^\circ$ ;  $V = 2031.0(7)$  Å<sup>3</sup>; ( $t = -150$  °C);  $M = 204.29$ ;  $Z = 8$ ;  $F(000) = 880$ ;  $\mu(\text{MoK}\alpha) = 2.9$   $\text{cm}^{-1}$ ;  $D_x = 1.336$   $\text{g cm}^{-3}$ . Absent reflections: ( $h0l$ ) for  $l$  odd, ( $0k0$ ) for  $k$  odd. Space group  $P2_1/c$  (No. 14).

## STRUCTURE DETERMINATION

The structure was determined by direct methods<sup>24</sup> and refined in the way described in Ref. 9. There are two molecules per asymmetric unit. The refinement converged to a conventional  $R$ -value of

0.050,  $R_w = 0.052$  and a goodness of fit,  $[\sum w\Delta F^2/(m-n)]^{1/2}$ , of 2.11.

Final atomic parameters are listed in Table 1. Tables of observed and calculated structure factors with standard deviations are available from the authors.

## RESULTS AND DISCUSSION

The geometry of the two molecules of the asymmetric unit is nearly identical; no chemically significant differences in bond lengths and bond angles nor in S–N torsion angles are apparent.

A drawing of a molecule is shown in Fig. 1, where the numbering of the atoms is also indicated. In Table 2 bond lengths, bond angles, torsion angles and various other structural data are given. Estimated standard deviations are calculated from the variance–covariance matrix. In Fig. 2 the Newman projection of the S–N bond in the average molecule is shown; the broken lines indicate approximate directions of the sulfur and nitrogen lone pairs. In Table 3 a comparison is made between the most relevant structural parameters (average values) in  $\text{Mor}_2\text{S}$ , determined in the present study, in  $(\text{MorS}-)_2$  and in  $(\text{MorS}_2-)_2$  from Refs. 16 and 17, respectively, in  $((\text{C}_6\text{H}_{11})_2\text{N})_2\text{S}$ <sup>18</sup> and in  $(\text{Me}_2\text{N})_2\text{S}$ .<sup>19</sup>

**Conformational considerations.** In the case of bis(dialkylamino)sulfides the preferential conformation seems to be a compromise between the operation of essentially two competing factors; the tendency of the sulfur and the nitrogen lone pairs to avoid each other and the opposing tendency to maximize dative  $p-d$   $\pi$  bonding.<sup>25,26</sup> This is apparently a quite common phenomenon in compounds with lone pairs on adjacent atoms, particularly for atoms from the upper part of the periodic system with lone pairs exhibiting some directional properties.<sup>27</sup> For a relevant comparison,

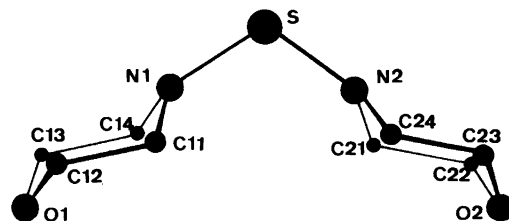


Fig. 1. Bis(morpholino)sulfide as seen normal to the NSN plane.

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by  $\exp[-2\pi^2(U_{11}a^*{}^2h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$ .

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
S1	0.10677(10)	0.26755(5)	0.63365(9)	0.0270(5)	0.0144(4)	0.0226(4)	-0.0010(5)	0.0092(4)	-0.0019(5)
S2	0.60145(10)	0.26104(5)	0.13867(9)	0.0223(5)	0.0160(4)	0.0289(5)	-0.0008(5)	0.0037(4)	0.0015(5)
O1	0.3079(3)	0.4437(2)	0.3963(3)	0.0372(17)	0.0242(15)	0.0357(16)	-0.0054(14)	0.0147(13)	0.0018(13)
O2	-0.0931(3)	0.4429(2)	0.8728(3)	0.0271(16)	0.0237(13)	0.0304(15)	0.0036(14)	0.0074(12)	-0.0024(14)
O3	0.3656(2)	0.4365(2)	-0.0697(2)	0.0284(16)	0.0238(15)	0.0339(17)	0.0014(12)	0.0000(13)	0.0028(13)
O4	0.8536(2)	0.4333(2)	0.3338(2)	0.0245(15)	0.0218(15)	0.0345(17)	-0.0001(11)	0.0058(12)	-0.0042(12)
N1	0.1854(3)	0.3279(2)	0.5413(3)	0.0232(17)	0.0215(17)	0.0210(16)	0.0010(14)	0.0081(14)	0.0025(13)
N2	0.0279(3)	0.3256(2)	0.7290(3)	0.0221(17)	0.0208(17)	0.0210(16)	0.0024(14)	0.0075(14)	-0.0012(13)
N3	0.5081(3)	0.3192(2)	0.0574(3)	0.0220(17)	0.0205(18)	0.0272(18)	0.0012(14)	0.0062(14)	0.0011(14)
N4	0.6989(3)	0.3203(2)	0.2139(3)	0.0182(16)	0.0252(19)	0.0249(17)	-0.0019(14)	0.0073(14)	-0.0028(14)
C11	0.1210(4)	0.3793(3)	0.4558(3)	0.0286(23)	0.0282(23)	0.0239(21)	-0.0003(19)	0.0063(18)	0.0045(18)
C12	0.2047(4)	0.3993(3)	0.3569(3)	0.0409(26)	0.0299(24)	0.0216(21)	0.0015(20)	0.0103(20)	0.0021(17)
C13	0.3705(4)	0.3925(3)	0.4778(4)	0.0249(22)	0.0298(24)	0.0402(25)	-0.0025(18)	0.0130(20)	-0.0026(19)
C14	0.2943(3)	0.3706(3)	0.5831(3)	0.0184(20)	0.0259(22)	0.0319(23)	-0.0027(17)	0.0074(18)	-0.0016(17)
C21	0.0936(4)	0.3746(3)	0.8166(3)	0.0251(21)	0.0236(21)	0.0218(20)	0.0008(17)	0.0052(17)	-0.0057(17)
C22	0.0091(4)	0.3972(3)	0.9137(4)	0.0356(25)	0.0316(25)	0.0255(22)	0.0100(20)	0.0054(20)	-0.0032(18)
C23	-0.1563(4)	0.3915(3)	0.7917(4)	0.0239(22)	0.0247(23)	0.0339(23)	0.0000(18)	0.0093(19)	-0.0003(18)
C24	-0.0790(3)	0.3700(3)	0.6885(3)	0.0231(21)	0.0261(22)	0.0264(21)	-0.0012(18)	0.0062(18)	-0.0004(17)
C31	0.4222(3)	0.3757(3)	0.1166(3)	0.0199(21)	0.0278(23)	0.0297(22)	-0.0024(18)	0.0076(18)	-0.0011(17)
C32	0.3220(4)	0.3966(3)	0.0331(4)	0.0212(21)	0.0295(23)	0.0361(24)	0.0029(17)	0.0029(19)	0.0039(18)
C33	0.4495(4)	0.3808(3)	-0.1258(3)	0.0339(22)	0.0245(22)	0.0277(22)	-0.0011(18)	0.0053(19)	0.0006(17)
C34	0.5532(4)	0.3599(3)	-0.0484(3)	0.0255(21)	0.0210(21)	0.0230(20)	-0.0022(17)	0.0073(17)	-0.0002(16)
C41	0.7919(3)	0.3689(3)	0.1519(3)	0.0209(20)	0.0213(21)	0.0263(21)	-0.0006(16)	0.0086(17)	0.0001(16)
C42	0.8935(3)	0.3868(3)	0.2348(3)	0.0202(20)	0.0231(22)	0.0330(22)	0.0008(16)	0.0079(18)	-0.0054(17)
C43	0.7640(4)	0.3852(3)	0.3935(3)	0.0298(22)	0.0207(21)	0.0272(21)	-0.0009(17)	0.0055(19)	-0.0015(16)
C44	0.6589(4)	0.3679(3)	0.3166(3)	0.0224(21)	0.0239(22)	0.0239(22)	0.0006(18)	0.0072(17)	-0.0015(17)

Atom	x	y	z	B	Atom	x	y	z	B
H111	0.096	0.432	0.493	2.2	H112	0.050	0.344	0.432	2.2
H121	0.162	0.434	0.300	2.2	H122	0.226	0.344	0.313	2.2
H131	0.444	0.423	0.050	2.2	H132	0.395	0.338	0.441	2.2
H141	0.276	0.429	0.625	2.2	H142	0.340	0.331	0.633	2.2
H211	0.124	0.431	0.783	2.2	H212	0.164	0.338	0.844	2.2
H221	0.051	0.433	0.969	2.2	H222	-0.018	0.339	0.952	2.2
H231	-0.226	0.426	0.766	2.2	H232	-0.177	0.338	0.832	2.2
H241	-0.060	0.424	0.649	2.2	H242	-0.119	0.336	0.632	2.2
H311	0.461	0.428	0.137	2.2	H312	0.389	0.348	0.183	2.2
H321	0.266	0.439	0.070	2.2	H322	0.279	0.340	0.012	2.2
H331	0.471	0.411	-0.201	2.2	H332	0.407	0.328	-0.148	2.2
H341	0.598	0.416	-0.026	2.2	H342	0.604	0.319	-0.088	2.2
H411	0.754	0.423	0.122	2.2	H412	0.820	0.335	0.090	2.2
H421	0.959	0.425	0.198	2.2	H422	0.925	0.326	0.258	2.2
H431	0.745	0.421	0.461	2.2	H432	0.796	0.328	0.424	2.2
H441	0.617	0.421	0.292	2.2	H442	0.604	0.331	0.360	2.2

cf. the structure of tris(dialkylamino)phosphines and arsines.<sup>9,10</sup>

In  $(R_2N)_2S$  several conformations are in principle possible, the three most conceivable ones having both the nitrogen lone pairs transoidal, one being

transoidal and one cisoidal, and finally both being cisoidal to the sulfur lone pairs.<sup>19</sup> Conformations based upon the direction of the lone pairs being perpendicular to the NSN plane seem to be highly sterically hindered. In all compounds of the general

Table 2. Structural data.

		Mol. A	Mol. B			Mol. A	Mol. B		
<b>Bond lengths (Å)</b>				<b>Bond angles (°)</b>					
S1	N1	1.679(3)	1.674(3)	N1	S1	N2	113.0(1)	113.3(1)	
S1	N2	1.683(3)	1.675(3)	S1	N1	C11	118.8(3)	118.2(3)	
N1	C11	1.463(5)	1.478(5)	S1	N1	C14	118.9(3)	119.2(3)	
C11	C12	1.515(6)	1.515(6)	N1	C11	C12	108.6(3)	108.4(3)	
C12	O1	1.424(5)	1.431(5)	C11	C12	O1	111.3(3)	111.7(3)	
O1	C13	1.421(6)	1.439(5)	C12	O1	C13	109.6(3)	109.6(3)	
C13	C14	1.529(6)	1.501(6)	O1	C13	C14	112.3(3)	111.6(3)	
C14	N1	1.472(5)	1.472(5)	C13	C14	N1	107.7(3)	108.9(3)	
N2	C21	1.468(5)	1.478(5)	C14	N1	C11	112.3(3)	110.6(3)	
C21	C22	1.514(6)	1.513(6)	S1	N2	C21	118.2(2)	119.5(3)	
C22	O2	1.429(5)	1.431(5)	S1	N2	C24	118.6(3)	120.0(2)	
O2	C23	1.423(5)	1.435(5)	N2	C21	C22	108.8(3)	108.5(3)	
C23	C24	1.516(6)	1.499(6)	C21	C22	O2	111.9(3)	111.4(3)	
C24	N2	1.462(5)	1.473(5)	C22	O2	C23	109.4(3)	109.9(3)	
				O2	C23	C24	111.1(3)	111.0(3)	
				C23	C24	N2	108.8(3)	109.3(3)	
				C24	N2	C21	112.4(3)	110.4(3)	
<b>Various averaged data</b>				<b>Torsion angles (°)</b>					
$\overline{S-N}$	(Å)	1.678(4)		N2	S1	N1	C11	-68.1(3)	-65.6(3)
$\overline{N-C}$	(Å)	1.470(6)		N2	S1	N1	C14	74.7(3)	73.7(3)
$\overline{C-C}$	(Å)	1.512(9)		N1	S1	N2	C21	-68.1(3)	-67.4(3)
$\overline{C-O}$	(Å)	1.429(6)		N1	S1	N2	C24	73.6(3)	74.6(3)
$\angle \overline{NSN}$	(°)	113.2(2)							
$\angle \overline{SNC}$	(°)	118.8(4)							
$\angle \overline{CNC}$	(°)	111.4(10)							
$\angle \overline{NCC}$	(°)	108.6(5)							
$\angle \overline{CCO}$	(°)	111.5(4)							
$\angle \overline{COC}$	(°)	109.6(2)							
Average sum of nitrogen bond angles: 349.5(5)°				Average deviation of N from plane SCC: 0.29(1) Å					
Average torsion angle N-S-N-Lone pair N: -176.6(6)°									

type  $(R_2N)_2S$  only the cisoidal conformation has so far been observed in the solid state; in the gas phase  $(Me_2N)_2S$  may contain some of the two other conformers.<sup>19</sup> A similar conformation has also been

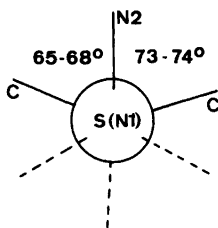


Fig. 2. Newman diagram of the S-N bond in bis(morpholino)sulfide.

observed for  $(Me_2N)_2SO$ <sup>28</sup> and for  $(Me_2N)_2SO_2$ .<sup>29</sup> Apparently, the determining factor is the tendency of the nitrogen lone pairs to be as far apart as possible and at the same time avoid the sulfur lone pairs in the divalent species and the oxygen atoms in the corresponding sulfoxides and sulfones.

As long as the cisoidal conformation is preferred, an ideal  $C_{2v}$  symmetry would favour a maximum overlap between a single sulfur  $d$ -orbital and the nitrogen  $p$ -orbitals since the axes of the nitrogen  $p$ -orbitals thus would be parallel. As a result, the four carbon atoms linked to the two nitrogen atoms would be coplanar as observed in  $[(C_6H_{11})_2N]_2S$ .<sup>18</sup> In  $Mor_2S$ , however, the two morpholino groups are twisted, and in opposite directions, some 10° away

Table 3. Comparison of some average structural parameters in  $\text{Mor}_2\text{S}_2$ ,  $(\text{MorS}-)_2$  ( $\text{MorS}-$ )<sub>2</sub>,  $[(\text{C}_6\text{H}_{11})_2\text{N}]_2\text{S}$  and  $(\text{Me}_2\text{N})_2\text{S}$ .

	$\text{Mor}_2\text{S}$	$(\text{MorS}-)_2$	$(\text{MorS}_2-)_2$	$[(\text{C}_6\text{H}_{11})_2\text{N}]_2\text{S}$	$(\text{Me}_2\text{N})_2\text{S}$
S-N	1.678(4)	1.685(4)	1.668(2)	1.657(4)	1.688(6)
$\Sigma \angle \text{N}^\circ$	349.5(5)	343-344	344-345	358-359	351(2)
$\angle \text{NSN}^\circ (\angle \text{NSS}^\circ)$	113.2(2)	(112)	[109.1(2)]	110.7(2)	114.5(16)
$\angle \text{CNS}^\circ$	118.8(4)	116(1)	116(1)	120(1)	117.9(6)
$\angle \text{CNC}$	111.4(10)	111(1)	112.1(3)	117.9(4)	116.5(16)
N-C	1.470(6)	1.47	1.462(6)	1.467	1.473(6)
Method	X-ray	X-ray	X-ray	X-ray	El.-diff.
Reference	This study	16	17	18	19

from the conformation of highest possible symmetry. Presumably, this twisting is caused by the hydrogen atoms on the carbon atoms linked to the nitrogen atoms. In the twisted form as observed in the present study four intramolecular H-H distances are in the range 2.45-2.52 Å.

*The N-S-N bond angle.* The N-S-N bond angle in  $\text{Mor}_2\text{S}$  and in comparable compounds, cf. Table 3, is slightly but significantly larger than the tetrahedral angle and considerably larger than the C-S-C bond angle in  $\text{R}_2\text{S}$  for which bond angles close to 100° are generally observed.<sup>30</sup> It has been suggested that the N-S-N angle is large because of repulsion between the partial double bonds between the central sulfur atom and the nitrogen atoms.<sup>18</sup> However, the spatial demands of a dialkylamino group will be better satisfied the larger the N-S-N bond angle is.

*Bond angles around the nitrogen atoms.* The sum of the bond angles around the nitrogen atoms,  $\Sigma \angle \text{N}$ , is 349.5(5)° in  $\text{Mor}_2\text{S}$ ; the given sum being the average of the four independent determinations, two for each of the two molecules in the asymmetric unit. The coordination of the nitrogen atoms is thus pyramidal, but the hybridization is closer to  $sp^2$  than to  $sp^3$ . The average distance from the nitrogen atoms to the plane through the three adjacent atoms is 0.29(1) Å.

In  $(\text{Me}_2\text{N})_2\text{S}$ <sup>19</sup> and in  $(\text{Me}_2\text{N})_2\text{SO}_2$ <sup>29</sup> a fairly similar hybridization of the nitrogen atoms is observed while in  $(\text{Mor}_2\text{S}-)_2$ ,<sup>16</sup> in  $(\text{Mor}_2\text{S}_2-)_2$ <sup>17</sup> and in  $(\text{Me}_2\text{N})_2\text{SF}_2$ <sup>26</sup> the nitrogen atoms have significantly more *p*-character,  $\Sigma \angle \text{N}$  being in the 343-345° range. In  $[(\text{C}_6\text{H}_{11})_2\text{N}]_2\text{S}$  and in  $\text{S}_7\text{NSNMe}_2$ <sup>17</sup> the nitrogen atoms are essentially  $sp^2$  hybridized,  $\Sigma \angle \text{N}$  being from 355° to 359°. The near planar geometry of the nitrogen atoms in

$[(\text{C}_6\text{H}_{11})_2\text{N}]_2\text{S}$  is apparently caused by the large CNC bond angle, 117.9(4)°, cf. Table 3, which presumably has its origin in the steric demands of the two cyclohexyl groups linked to the same nitrogen atom.

*The sulfur nitrogen bond length.* A number of X-ray, electron diffraction and microwave studies on compounds with S-N bonds have appeared in recent years. In non-charged species the S-N bond length is presently known to cover a larger range, from 1.446 Å in  $\text{F}_3\text{SN}$ <sup>31</sup> to 1.90 Å for the axial bond in a spirocyclic sulfuran.<sup>32</sup> For surveys of S-N bond lengths, cf. Refs. 33 and 34. The exceptional large range for the S-N bond length observed may suggest that this bond length is even more sensitive to the oxidation state of the central atom and of the hybridization of the nitrogen atom than is the P-N bond in phosphorus-nitrogen compounds.<sup>9,35</sup>

According to the Stevenson-Schomaker equation<sup>36</sup> the S-N single bond is 1.735 Å, which is the same length as the P-N single bond.<sup>37</sup> In  $\text{Mor}_2\text{S}$ , as observed in the present study, the average S-N bond length is 1.678(4) Å indicating a bond order of approximately 1.1.<sup>38</sup> It is notable that the S-N bond lengths in  $\text{Mor}_2\text{S}$  are as in several other compounds, cf. Table 3, but are significantly longer than in  $[(\text{C}_6\text{H}_{11})_2\text{N}]_2\text{S}$ , 1.657(4) Å.<sup>18</sup> Presumably, this difference is due to the difference in the hybridization of the nitrogen atoms in  $\text{Mor}_2\text{S}$  and in  $[(\text{C}_6\text{H}_{11})_2\text{N}]_2\text{S}$  combined with the lack of  $C_{2v}$  symmetry in  $\text{Mor}_2\text{S}$ . Since the four carbon atoms linked to the two nitrogen atoms are not coplanar the nitrogen *p*-orbitals will not have the ideal direction for maximum overlap with a sulfur *d*-orbital. As a result, the delocalization of the nitrogen lone pairs onto the sulfur atom is limited and causing the nitrogen atoms to retain much of their

$sp^3$  hybridization. The S—N bond length is thus only slightly shorter than the S—N single bond length.

*Intramolecular contacts.* The shortest distances between the hydrogen atoms are in the range 2.45—2.52 Å. There is little doubt that these contacts are of importance both for the magnitude of the N—S—N angle and for the torsion angles about the S—N bonds. As may be seen from Table 2 the torsion angles about the four non-equivalent S—N bonds are nearly equal; this is also depicted in the Newman diagram in Fig. 2.

*The structure of the substituents.* The morpholino substituents are in the expected chair conformation and linked equatorially to the central sulfur atom. The bond lengths and the bond angles listed in Table 2 are all of the expected magnitude.

## CONCLUSIONS

Bis(dialkylamino)sulfides,  $(R_2N)_2S$ , seem to prefer a conformation by which the nitrogen lone pair are cisoidal to the sulfur lone pairs. For substituents of sufficiently small steric demands the molecules may attain a  $C_{2v}$  symmetry whereby the nitrogen  $p$ -orbitals are parallel and well suited for interaction with a sulfur  $d$ -orbital through  $d_\pi-p_\pi$  overlap. In less symmetrical compounds, as in  $Mor_2S$ , the  $d_\pi-p_\pi$  overlap is not maximized, resulting in longer S—N bonds and more pyramidal nitrogen atoms. The reactivity pattern of bis(dialkylamino)sulfides may thus be significantly dependent upon the steric demands of the substituents linked to the nitrogen atoms.

The weak nucleophilicity of the sulfur atom in  $(R_2N)_2S$  has its probable background in the large N—S—N bond angle,  $\sim 113^\circ$ . The presence of nitrogen atoms of some  $sp^3$  character is in agreement with the observation that this class of compounds may act as nitrogen donors toward certain Lewis acids. The weak nucleophilicity of the central sulfur atom combined with its ability to undergo insertion reactions with  $CS_2$  and other species<sup>39</sup> suggests that chemically  $(R_2N)_2S$  resembles  $(R_2N)_3As$ <sup>10</sup> far more than  $(R_2N)_3P$ .<sup>9</sup> It is presently not known whether  $(R_2N)_2S$  acts as biphilic species toward  $CS_2$  or if the insertion product is formed through a multistep mechanism. However, the fairly low torsional barrier about the S—N bond in  $(R_2N)_2S$ <sup>14</sup> may allow these compounds to easily adapt to any necessary conformation in solution, especially at elevated temperatures.

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