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Various 2-substituted-4,6-bis(alkylamino)-1,3,5-triazines, **1**, have been found to react with alkoxy carbonylsulfonyl chlorides, **2**, to give the title compounds, **3**. The structural characterization of **3a** in the solid state by single X-ray crystallographic analysis established that it is the isomer wherein the methoxycarbonylthio group is attached to the less sterically hindered, exocyclic nitrogen bearing the ethyl group.

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### Introduction.

Alkoxy carbonylsulfonyl chlorides [1,2] are highly reactive electrophilic thiocarboxylating reagents as shown by their reaction with substituted 4-amino-1,2,4-triazin-5(4*H*)-ones [3]. Trichloromethanesulfonyl chloride ("perchloromethyl mercaptan") is the only sulfonyl halide which has been used to prepare *N*-(trichloromethyl)sulfonylated 2-chloro-4,6-bis(alkylamino)-*s*-triazines patented as herbicides [4]. Since 2-chloro-4,6-bis(alkylamino)-*s*-triazines are an important class of herbicides, we prepared a number of *N*-(alkoxy carbonylsulfonyl) derivatives. Alkoxy carbonylsulfonylation of diamino-*s*-triazines may in principle give products involving either one of the two exocyclic or one of the three ring-nitrogen atoms. Since some of the *N*-(alkoxy carbonylsulfonyl)-*s*-triazines have desirable physical and herbicidal properties [5], their actual structures are of particular interest. Because their structure could not be unequivocally established from conventional spectroscopic analyses, we undertook a study of the conformational properties of **3a** in the solid state. The results are described below.

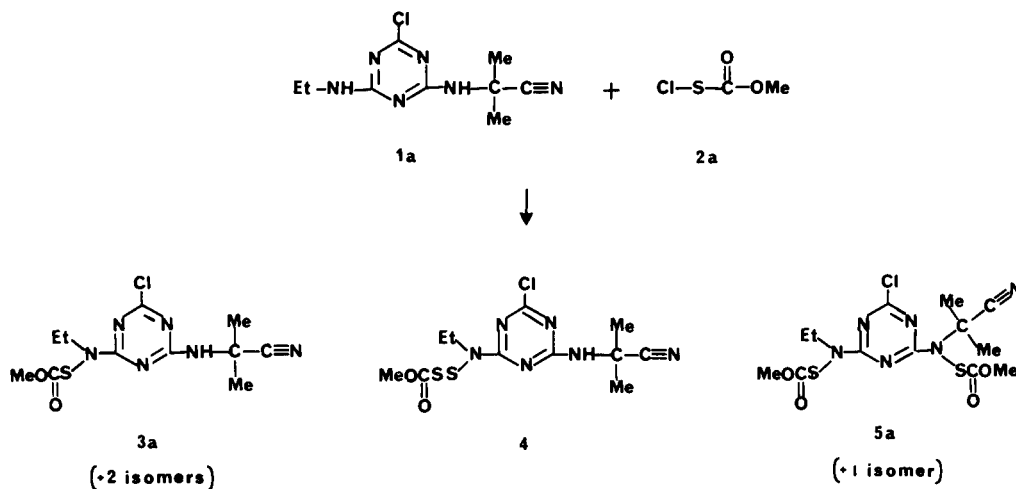
### Results and Discussions.

#### *N*-(Alkoxy carbonyl)sulfonylations.

As typical  $\alpha$ -amino-*N*-heterocyclic compounds with guanidine structure, *s*-triazines **1** may undergo sulfonylation reaction to give products involving either exocyclic or ring-nitrogen atoms. For example, the condensation of chloroformylsulfonyl chloride with five-membered  $\alpha$ -amino-*N*-heterocyclic compounds has been shown to give two isomeric products when carried out in different solvents [6,7]. When the sulfonylation was carried out in a proton-acceptor solvent, *e.g.*, tetrahydrofuran, which tends to solvate the exocyclic amino group, the ring-nitrogen atom was sulfonylated, whereas the exocyclic nitrogen atom was sulfonylated in the proton-donor solvent, chloroform, which tends to solvate the ring-nitrogen leaving the exocyclic amino group free to react.

For example, when the triazine **1a** (cyanazine [8]) was allowed to react with methoxycarbonylsulfonyl chloride **2a** in the molar ratio of 1:1.5 in methylene chloride at 0-5° and in the presence of Hünig's base (1.5 molar equivalents), the structure shown in Scheme 1 was assigned to the

Scheme 1

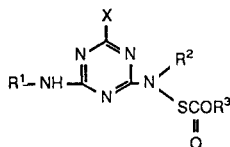




only isolated product **3a** (18% yield). Steric considerations would favor structure **3a** over one in which the sulfonyl group is linked to the second, sterically more hindered exocyclic nitrogen. Sulfonylation of ring-nitrogen of **1a** appeared unlikely based upon the argument presented above. Furthermore, spectroscopic studies have shown that  $\alpha$ -amino-*N*-heterocyclic compounds usually exist in all media predominantly in the amino form [9].

The structural assignment of **3a** became ambiguous when subsequent experiments on larger scale under milder conditions ( $-15^\circ$ ) yielded **3a**, the disulfide **4**, the bis(sulfonylated) triazine **5** and, in small amounts, two constitutional isomers of **3a** (by gc-ms). In the absence of rigorous structure proof of the bis(sulfonylated) triazine, the structure of **5** is tentative (Scheme 1).

The *s*-triazine herbicides **1b** (atrazine [8]), **1c** (simazine

Table 1.  
*N*-(Alkoxy carbonylsulfonyl)-*s*-Triazines, **3**

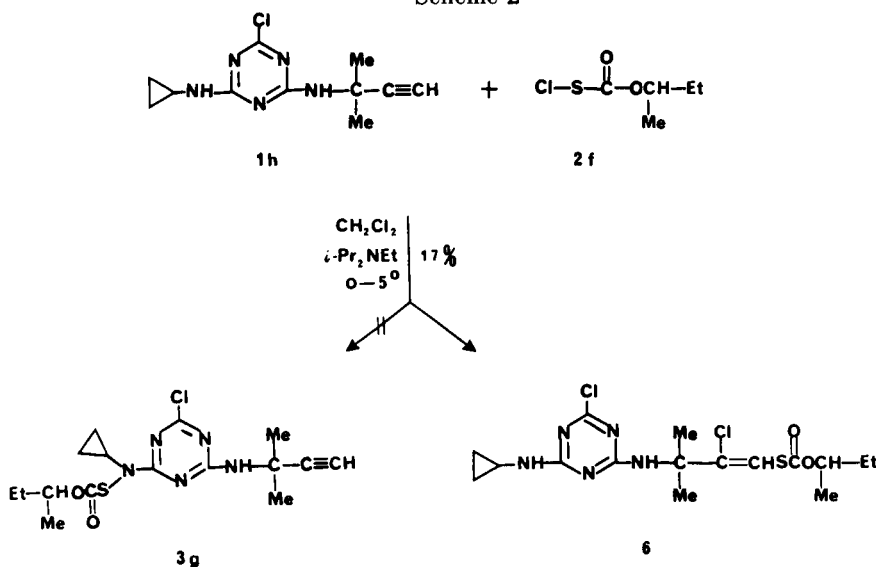


No. of Starting Materials	Product	X	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	% Yield	mp, °C	Formula (Molecular Weight)	Carbon Calcd. Found	Hydrogen Calcd. Found	Nitrogen Calcd. Found	EI-MS (M <sup>+</sup> )	
1a	2a	3a	Cl	C(CH <sub>3</sub> ) <sub>2</sub> CN	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	18	95-97	C <sub>11</sub> H <sub>15</sub> ClN <sub>6</sub> O <sub>2</sub> S (330.79)	39.9 39.8	4.6 4.5	25.4 25.4	330
1a	2b	3b	"	"	"	C <sub>2</sub> H <sub>5</sub>	37	[a]	C <sub>12</sub> H <sub>17</sub> ClN <sub>6</sub> O <sub>2</sub> S (344.80)	41.8 41.6	5.0 4.8	24.4 24.5	344
1a	2d	3c	"	"	"	CH(CH <sub>3</sub> ) <sub>2</sub>	39	[a]	C <sub>13</sub> H <sub>19</sub> ClN <sub>6</sub> O <sub>2</sub> S (358.84)	43.5 43.8	5.3 5.6	23.4 24.2	358
1a	2f	3d	"	"	"	CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	4	[a]	C <sub>14</sub> H <sub>21</sub> ClN <sub>6</sub> O <sub>2</sub> S (372.81)	45.1 44.9	5.7 5.5	22.5 22.2	372 [b]
1a	2g	3e	"	"	"	C(CH <sub>3</sub> ) <sub>3</sub>	1	[a]	C <sub>14</sub> H <sub>21</sub> ClN <sub>6</sub> O <sub>2</sub> S (372.81)	45.1 44.8	5.7 5.5	22.5 22.3	373 [b]
1b	2a	3f	"	CH(CH <sub>3</sub> ) <sub>2</sub>	"	CH <sub>3</sub>	36	[a]	C <sub>10</sub> H <sub>16</sub> ClN <sub>5</sub> O <sub>2</sub> S (305.78)	39.3 39.6	5.3 5.6	22.9 22.5	305
1b	2b	3g	"	"	"	C <sub>2</sub> H <sub>5</sub>	34	[a]	C <sub>11</sub> H <sub>18</sub> ClN <sub>5</sub> O <sub>2</sub> S (319.81)	41.3 41.3	5.7 5.8	21.9 21.9	319
1b	2f	3h	"	"	"	CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	25	[a]	C <sub>13</sub> H <sub>22</sub> ClN <sub>5</sub> O <sub>2</sub> S (345.85)	45.1 45.5	6.4 6.7	20.2 20.0	348 [b]
1b	2g	3i	"	"	"	C(CH <sub>3</sub> ) <sub>3</sub>	2	[a]	C <sub>13</sub> H <sub>22</sub> ClN <sub>5</sub> O <sub>2</sub> S (345.85)	45.1 45.4	6.4 6.4	20.2 20.0	348 [b]
1c	2a	3j	"	C <sub>2</sub> H <sub>5</sub>	"	CH <sub>3</sub>	23	95-97	C <sub>9</sub> H <sub>14</sub> ClN <sub>5</sub> O <sub>2</sub> S (291.75)	37.1 37.1	4.8 4.9	24.0 24.0	291
1c	2f	3k	"	"	"	CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	17	80-83	C <sub>12</sub> H <sub>20</sub> ClN <sub>5</sub> O <sub>2</sub> S (333.84)	43.2 43.3	6.0 6.2	21.0 20.9	333
1d	2f	3l	"	CH(CH <sub>3</sub> ) <sub>2</sub>		"	29	[a]	C <sub>14</sub> H <sub>22</sub> ClN <sub>5</sub> O <sub>2</sub> S (359.87)	46.7 46.4	6.2 5.9	19.5 19.6	359
1d	2h	3m	"	"	"	CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>13</sub>	36	[a]	C <sub>18</sub> H <sub>30</sub> ClN <sub>5</sub> O <sub>2</sub> S (415.98)	52.0 52.2	7.3 7.5	16.8 16.5	415
1e	2a	3n	OCH <sub>3</sub>	"	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	42	[a]	C <sub>11</sub> H <sub>19</sub> N <sub>5</sub> O <sub>2</sub> S (301.36)	43.8 43.7	6.4 6.3	23.2 23.5	301
1f	2a	3o	SCH <sub>3</sub>	"	"	"	46	[a]	C <sub>11</sub> H <sub>19</sub> N <sub>5</sub> O <sub>2</sub> S <sub>2</sub> (317.72)	41.6 41.5	6.0 6.0	22.1 21.7	317
1g	2a	3p	OCH <sub>3</sub>	"		"	34	77-80	C <sub>11</sub> H <sub>19</sub> N <sub>5</sub> O <sub>3</sub> S (301.36)	46.0 46.1	6.1 6.2	22.3 22.3	313

[a] Amber syrup liquid.

[b] CI-MS: (M+H)<sup>+</sup>.

Scheme 2



[8]), **1d** (cyprazine [8]), **1e** (atratone [8]), **1f** (ametryn [8]), and **1g** reacted analogously with alkoxy-carbonylsulfenyl chlorides **2a-2h** (Table 8) in methylene chloride and in the presence of one molar equivalent of Hünig's base to give *N*-(alkoxy-carbonylsulfenylated)-*s*-triazines (Table 1). A departure from these sulfenylation reactions was observed when the acetylenic triazine **1h** was allowed to react with **2f**. None of the expected substitution product **3q** was detected in the reaction mixture; the product and isolated in 15% yield was **6**, formed by the addition of **2f** across the triple bond of **1h**. The structure of **6** is based on the mass spectrum which shows  $m/z$  385 ( $M^+ - \text{Cl}$ ), and the  $^1\text{H}$  nmr spectrum, which is indicative of the presence in the molecule of two NH-protons ( $\delta$  5.52 (NH) and 5.81 (NH)).

Throughout this work, the assumption was made that the entering alkoxy-carbonylsulfenyl group would attach itself onto the least sterically hindered nitrogen atom of the alkylamino substituent. Since unequivocal structure proof by spectroscopic methods was not possible for compounds **3**, we undertook a crystallographic study of the structure of **3a**.

#### X-Ray Crystallographic Analysis.

Crystals of **3a** are monoclinic with space group  $P2_1/n$ . Details of the X-ray crystallographic analysis and unit cell are given in the Experimental and in Tables 2 and 3. An ORTEP plot of the X-ray crystallographic structure is shown in Figure 1. The unit cell packing structure and a stereoscopic view of the unit cell are shown in Figures 2 and 3. The bond distances, bond angles, and torsional angles are listed in Tables 4, 5, and 6.

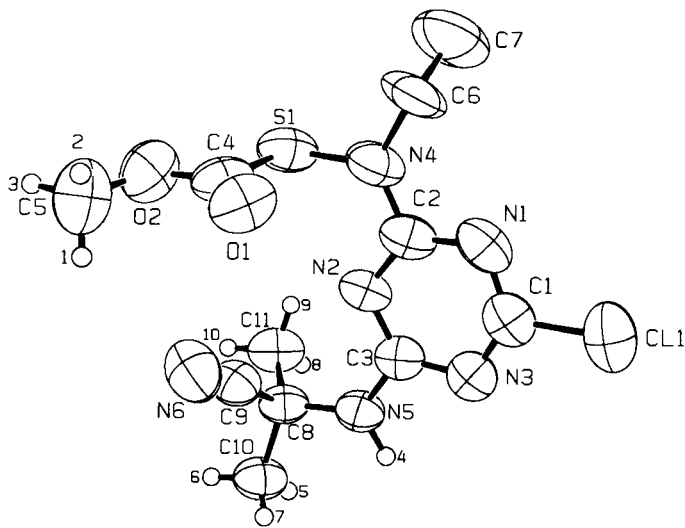


Figure 1

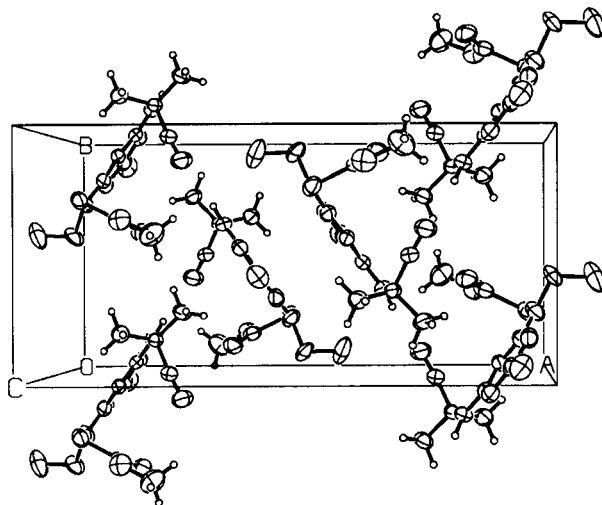


Figure 2

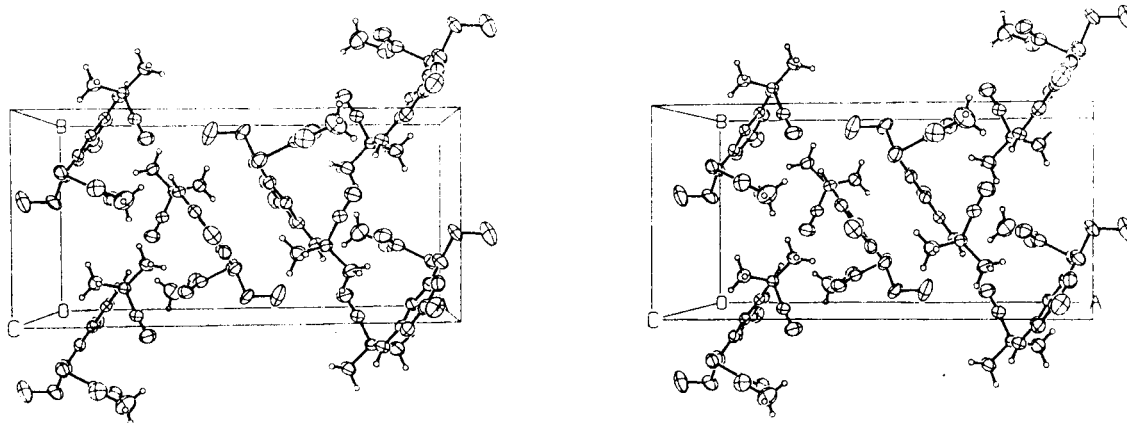


Figure 3

Table 2

## Crystallographic Data

Compound:	<b>3a</b>
Molecular formula:	$C_{11}H_{15}ClN_6O_2S$
Formula weight:	330.79
Space group:	Monoclinic $P2_1/n$
Calculated density ( $\rho$ ):	1.36 g/cm <sup>3</sup>
Cell Dimensions:	$a = 18.870 (6) \text{ \AA}$ $b = 9.161 (3) \text{ \AA}$ $c = 9.437 (2) \text{ \AA}$ $B = 96.74 (3) \text{ deg}$ $Z = 4$ $V = 1620 (2) \text{ \AA}^3$

Table 3

## Structure Solution and Refinement

Solution:	Direct methods
Hydrogen atoms:	Included in calculated positions
Refinement:	Full-matrix least-squares
Minimization function:	$\sum w ( F_o  -  F_c )^2$
Least-squares weights:	$4F_o^2/\sigma^2(F_o^2)$
"Ignorance" factor:	0.050
Anomalous dispersion:	All non-hydrogen atoms
Reflections included:	1773 with $F_o^2 > 3.0 \sigma(F_o^2)$
Parameters refined:	197
Unweighted agreement factor:	0.066
Weighted agreement factor:	0.097
Factor including unobs. data:	0.096
Esd of obs. of unit weight:	2.51
Convergence, largest shift:	0.04 $\sigma$
High peak in final difference map:	0.85 e/ $\text{\AA}^3$
Computer hardware/software:	Vax based Texray computer system with the Texsan software package

Table 4

## Selected Bond Distances [17]

Atom	Atom	Distance	Atom	Atom	Distance
CL1	C1	1.728(6)	N4	C2	1.376(7)
S1	N4	1.673(5)	N4	C6	1.54(1)
S1	C4	1.792(7)	N4	C6D	1.65(5)
O1	C4	1.202(7)	N5	C3	1.331(6)
O2	C4	1.327(7)	N5	C8	1.454(6)
O2	C5	1.43(1)	N6	C9	1.133(7)
N1	C1	1.335(7)	C6	C7	1.47(2)
N1	C2	1.354(7)	C8	C9	1.460(7)
N2	C2	1.315(7)	C8	C11	1.524(7)
N2	C3	1.334(6)	C8	C10	1.527(7)
N3	C1	1.276(7)	C6D	C7D	1.57(4)
N3	C3	1.347(6)			

Table 5

## Selected Bond Angles [18]

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N4	S1	C4	100.7(3)	N1	C2	N4	116.9(5)
C4	O2	C5	116.0(5)	N5	C3	N2	117.4(5)
C1	N1	C2	112.1(5)	N5	C3	N3	117.1(5)
C2	N2	C3	114.6(5)	N2	C3	N3	125.4(5)
C1	N3	C3	113.2(5)	O1	C4	O2	127.2(6)
C2	N4	C6	121.6(7)	O1	C4	S1	124.9(6)
C2	N4	C6D	119(1)	O2	C4	S1	107.9(4)
C2	N4	S1	119.9(4)	C7	C6	N4	110(1)
C6	N4	S1	117.6(6)	N5	C8	C9	109.0(4)
C6D	N4	S1	119(1)	N5	C8	C11	112.2(5)
C3	N5	C8	124.7(4)	N5	C8	C10	107.1(4)
N3	C1	N1	129.2(6)	C9	C8	C11	109.5(4)
N3	C1	CL1	117.1(5)	C9	C8	C10	108.2(5)
N1	C1	CL1	113.7(5)	C11	C8	C10	110.7(4)
N2	C2	N1	125.5(5)	N6	C9	C8	174.9(6)
N2	C2	N4	117.7(6)	C7D	C6D	N4	95(3)

Table 6  
Torsion or Conformation Angles [19]

(1)	(2)	(3)	(4)	Angle	(1)	(2)	(3)	(4)	Angle
CL1	C1	N3	C3	179.5(4)	N5	C3	N2	C2	178.8(4)
CL1	C1	N1	C2	-178.6(3)	N5	C3	N3	C1	-177.8(4)
S1	N4	C2	N2	-2.7(7)	N5	C8	C9	N6	-110(7)
S1	N4	C2	N1	178.5(4)	N5	C8	C11	H9	-59.70
S1	N4	C6	C7	-85.0(1)	N5	C8	C11	H8	62.18
S1	N4	C6D	C7D	76.0(2)	N5	C8	C11	H10	-178.91
S1	C4	O2	C5	177.9(5)	N5	C8	C10	H7	57.42
O1	C4	O2	C5	-2.4(9)	N5	C8	C10	H6	178.01
O1	C4	S1	N4	0.7(6)	N5	C8	C10	H5	-68.39
O2	C4	S1	N4	-179.6(4)	N6	C9	C8	C11	127(7)
N1	C1	N3	C3	-1.3(8)	N6	C9	C8	C10	6(7)
N1	C2	N2	C3	-0.9(7)	C2	N4	C6	C6D	91(4)
N1	C2	N4	C6	-13.0(1)	C2	N4	C6	C7	107(1)
N1	C2	N4	C6D	17.0(2)	C2	N4	C6D	C7D	-122(2)
N2	C2	N1	C1	-0.9(7)	C2	N4	S1	C4	83.8(5)
N2	C2	N4	C6	165.5(8)	C3	N5	C8	C9	-53.6(6)
N2	C2	N4	C6D	-164.0(2)	C3	N5	C8	C11	67.9(6)
N2	C3	N5	H4	174.48	C3	N5	C8	C10	-170.4(5)
N2	C3	N5	C8	-5.3(7)	C4	O2	C5	H2	50.80
N2	C3	N3	C1	-1.0(7)	C4	O2	C5	H3	174.09
N3	C1	N1	C2	2.2(8)	C4	O2	C5	H1	-69.12
N3	C3	N5	H4	-8.48	C4	S1	N4	C6	-84.9(7)
N3	C3	N5	C8	171.8(4)	C4	S1	N4	C6D	-114.0(2)
N3	C3	N2	C2	2.0(7)	C6	N4	C6D	C7D	-18.0(2)
N4	C2	N2	C3	-179.6(5)	C10	C8	N5	H4	9.85
N4	C2	N1	C1	177.8(5)	C10	C8	C11	H9	-179.30
C9	C8	N5	H4	126.67	C10	C8	C11	H8	-57.42
C9	C8	C11	H9	61.46	C10	C8	C11	H10	61.49
C9	C8	C11	H8	-176.65	C11	C8	N5	N5	H4 11.84
C9	C8	C11	H10	-57.75	C11	C8	C10	H7	-179.96
C9	C8	C10	H7	-59.91	C11	C8	C10	H6	-59.37
C9	C8	C10	H6	60.68	C11	C8	C10	H5	59.23
C9	C8	C10	H5	179.27					

These data clearly show that the alkoxy carbonylthio group is attached to the less sterically hindered, exocyclic nitrogen N-4 bearing the ethyl group. As would be expected, the triazine ring is planar (Table 7). With one exception, the carbon-nitrogen bond distances in the triazine ring fall in the range of 1.32-1.35 Å which are consistent with C-N double bonds [10]. The one exception is the C(1)-N(3) bond which is slightly shorter, 1.28 Å. The reason for this decreased bond length is not clear. An additional planar region involves the methoxy carbonylthio

side chain. This plane is comprised of N-4, S(1), C(4), O(1), O(2), and C(5) (Table 7). The dihedral angle between this plane and the triazine ring is 98°. The ethyl group attached to the exocyclic nitrogen N-4 was found to be disordered.

#### X-Ray Crystallographic Analysis of **3a** [11].

##### Data Collection.

A colorless parallelepiped crystal of **3a**, C<sub>11</sub>H<sub>15</sub>ClN<sub>6</sub>O<sub>2</sub>S, having approximately dimensions of 0.50 × 0.50 × 0.50

Table 7

Distances (Å) from the Best Planes through C1, N1, C2, N2, C3, N3 (A) and N4, S1, C4, O1, O2, C5 (B)

Atom	Plane A		Plane B	
	Distance	Atom	Distance	Atom
Atoms in Plane				
C1	-0.0123 (.0051)	N4	-0.0129 (.0046)	
N2	0.0089 (.0044)	S1	0.0009 (.0015)	
C2	0.0005 (.0052)	C4	0.0031 (.0053)	
N2	-0.0083 (.0039)	O1	0.0080 (.0040)	
C3	0.0113 (.0046)	O2	0.0049 (.0047)	
N3	-0.0001 (.0041)	C5	-0.0411 (.0090)	

Additional Atoms

CL1	-0.0402
N4	-0.0263
N5	-0.0220

Numbers in parenthesis are estimated standard deviations in the least significant digits.

mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å) on a Rigaku AFAC5 diffractometer equipped with a graphite crystal; incident beam monochromator and a 12 KW rotating anode generator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range of  $5 < \theta < 13^\circ$ , measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are:

$$a = 18.870(6) \text{ \AA} \quad b = 9.161(3) \text{ \AA} \quad c = 9.437(2) \text{ \AA}$$

$$\beta = 96.74(3)^\circ$$

$$v = 1620(2) \text{ \AA}^3$$

For  $Z = 4$  and  $F. W. = 330.68$ , the calculated density is  $1.36 \text{ g/cm}^3$ . As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-weight was  $0.25^\circ$  with a take-off angle of  $6.0^\circ$ , indicating good crystal quality. Based on the systematic absences of:

$$OkO: k = 2n + 1$$

$$HOl: h + 1 = 2n + 1$$

and from subsequent least-squares refinement, the space group was determined to be:

$$P2_1/n \text{ (#14)}$$

The data were collected at a temperature of  $23^\circ \pm 1^\circ$  using the  $\omega$ - $\theta$  scan technique. The scan rate was  $48^\circ/\text{minute}$  (in  $\theta$ ). The weak reflections ( $1 < 10 \text{ sig}(1)$ ) were rescanned (maximum of 3 rescans), and the counts were accumulated to assure good counting statistics. Data were collected to a maximum  $2\theta$  of  $140.0^\circ$ . The scan range (in  $^\circ$ ) was determined as a function of  $\theta$  to correct for the separation of the K $\alpha$  doublet [12]; the scan width was calculated as follows:

$$\theta \text{ scan width} = 1.5 + 0.300 \tan \theta$$

Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 40 cm.

#### Data Reduction.

A total of 3296 reflects were collected of which 2980 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured after every 200 reflections. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is  $33.7 \text{ cm}^{-1}$  for Cu K $\alpha$  radiation. No absorption correction was made. An extinction correction was not necessary.

#### Structure Solution and Refinement.

The structure was solved by direct methods. The ethyl group (C6 and C7) was found to be disordered. Occupancy factors for the two components were assigned as 0.7 and 0.3 based on the relative heights of difference Fourier peaks associated with these atoms. Hydrogen atoms were located and added to the structure factor calculations with idealized geometries and assigned isotropic thermal parameters ( $1.2 \times \text{Beq}$  of host atom), but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was  $\sum w (|F_o| - |F_c|)^2$ . The weight  $w$  is defined as  $4F_o^2/\sigma^2 F_o^2$ .

The standard deviation on intensities,  $(F_o^2)$ , is defined as follows:

$$\sigma^2(F_o^2) = [S^2 (C = R^2B) + (pF_o^2)^2]/Lp^2$$

where  $S$  is the scan rate,  $C$  is the total integrated peak count,  $R$  is the ratio of scan time to background counting time,  $B$  is the total background count,  $Lp$  is the Lorentz-polarization factor, and the parameter  $p$  is a factor introduced to downweight intense reflections. Here  $p$  was set to 0.05.

Scattering factors were taken from Cromer and Waber [13]. Anomalous dispersion effects were included in  $F_c$ ; <sup>14</sup> the values for  $f'$  and  $f''$  were those of Cromer [15].

Only the 1773 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 197 variable parameters and converted (largest parameter shift was 0.04 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.066$$

$$R2 = \text{SQRT} \left( \frac{\sum w (|F_o| - |F_c|)^2}{\sum w F_o^2} \right) = 0.097$$

The standard deviation of an observation of unit weight was 2.51. The highest peak in the final difference Fourier had a height of 0.85 e/A and was located in the vicinity of the disordered ethyl group. Plots of  $\sum w (|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin(\theta)/\lambda$ , and various classes of indices showed no unusual trends.

All calculations were performed on a Vax based Texray [16] system, a powerful laboratory computer system which includes the Texsan crystallographic software package of Molecular Structure Corporation.

## EXPERIMENTAL

### General Methods.

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected, as are boiling points. Routinely, reaction courses and product mixtures were monitored by thin layer chromatography (tlc) or gas-liquid chromatography (glc). Thin layer

separations were accomplished on silica gel GF<sup>254</sup> plates with visualization by iodine vapor, phosphomolybdic acid spray, or uv light. Infrared (ir) spectra were measured on a Digilab FTS-15E or Beckman Acculab I spectrophotometer, and only pertinent and other strong absorptions are listed. Bruker WM-360 or General Electric QE-300 spectrometers were used to obtain nuclear magnetic resonance (nmr) data. Peak positions are given in ppm downfield from tetramethylsilane as an internal standard. Mass spectra were determined at 70 eV on a Finnigan 4000 spectrometer, either through gas chromatographic (gc-ms) or solid probe sample introduction, and only the pertinent or more abundant fragment peaks are recorded. In the absence of clearly detectable molecular ions chemical ionization using  $\text{CH}_4$  was employed on the same instrument.

### Alkoxycarbonylsulfonyl Chlorides (2).

These were prepared according to published methods. The first (method A) consists of the reaction of chlorocarbonylsulfonyl chloride with an alcohol [1]. This method gave good to excellent results with primary alcohols, but the method failed with secondary and tertiary alcohols. For the compounds **2** derived from a secondary and tertiary alcohol, we applied the cleavage by chlorine of unsymmetrically diacyl sulfides [2] (method B in Table 8).

### Potassium O-(1-methylpropyl)thiocarbonate.

Potassium (9.45 g, 2.42 g-atoms) was added in portions to 1500 ml of 2-butanol under nitrogen, the temperature of the mixture being allowed to rise from room temperature to 85°. The resulting solution was cooled to 15° and 162.0 g (2.7 mole) of carbonyl sulfide was introduced with stirring. The resulting mixture was stirred at room temperature for 2 hours, diluted with 1000 ml of ether, and filtered. The solid was washed with ether and dried to give 387.0 g (93%) of off-white solid, mp 230-240° with dec; ir (potassium bromide): 3000-2800 (-CH), 1597 (C=O, thiocarbonate), and 1200-1000 (C-OC)  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_5\text{H}_9\text{O}_2\text{SK}$  (172.27): C, 34.8; H, 5.3; S, 18.6. Found: C, 34.6; H, 5.3; S, 18.8.

### Acetyl 2-Butoxycarbonyl Sulfide.

To a stirred and cooled (-15°) suspension of 395.0 g (2.3 moles) of the above salt in 1500 ml of methylene chloride was added dropwise over 2

Table 8  
(Alkoxycarbonyl)sulfonyl Chlorides **2**

Number of Compound	R	% Yield	BP. °C (mm Hg)	Method	Ref	Formula	(Mol. Weight)	Analysis	
								Carbon Calcd. Found	Hydrogen Calcd. Found
<b>2a</b>	CH <sub>3</sub>	69	56-60 (40-50)	A	[20]	C <sub>2</sub> H <sub>3</sub> ClO <sub>2</sub> S	(126.56)	19.0	2.4
								19.2	2.0
<b>2b</b>	C <sub>2</sub> H <sub>5</sub>	58	45-47 (15)	A	[20]	C <sub>3</sub> H <sub>5</sub> ClO <sub>2</sub> S	(140.58)	25.6	3.6
								25.8	3.4
<b>2d</b>	CH(CH <sub>3</sub> ) <sub>2</sub>	50	65-70 (35-40)	B	—	C <sub>4</sub> H <sub>7</sub> ClO <sub>2</sub> S	(152.59)	31.5	3.3
								31.7	3.2
<b>2c</b>	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	54	105-110 (100)	A	[20]	C <sub>4</sub> H <sub>7</sub> ClO <sub>2</sub> S	(154.61)	31.1	4.6
								31.1	4.7
<b>2f</b>	CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	78	45-46 (3)	B	—	C <sub>5</sub> H <sub>9</sub> ClO <sub>2</sub> S	(168.64)	35.6	5.4
								35.3	5.6
<b>2g</b>	C(CH <sub>3</sub> ) <sub>3</sub>	59	38-40 (1.5)	B	[21]	C <sub>5</sub> H <sub>9</sub> ClO <sub>2</sub> S	(168.64)	35.6	5.4
								35.3	5.2
<b>2e</b>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	68	105-110 (60)	A	—	C <sub>5</sub> H <sub>9</sub> ClO <sub>2</sub> S	(168.64)	35.6	5.4
								35.6	5.5
<b>2h</b>	CH(CH <sub>3</sub> )C <sub>6</sub> H <sub>13</sub>	91	—	B	—	C <sub>9</sub> H <sub>17</sub> ClO <sub>2</sub> S	(224.74)	48.1	7.6
								48.4	7.6

hours 188.4 g (2.4 moles) of acetyl chloride. The mixture was stirred at  $-15^{\circ}$  to  $-5^{\circ}$  for 2 hours, then at  $0^{\circ}$  for 3 hours, then at ambient temperature for 18 hours. The reaction mixture was filtered and the filtrate concentrated at  $30^{\circ}$  (30 mm Hg) to give 372.8 g (92%) of pale yellow oil, bp  $65-67^{\circ}$  (0.4 mm); ir (methylene chloride): 3000-2800 (C-H), 1771-1709 (C=O), 1200-1000 (C-OC)  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_7\text{H}_{12}\text{O}_3\text{S}$  (176.23): C, 47.7; H, 6.9. Found: C, 47.5; H, 7.1.

#### 2-Butoxycarbonylsulfonyl Chloride (2f).

To a stirred and cooled ( $-15^{\circ}$ ) solution of 372.0 (2.11 mole) of the above acetyl sulfide in 1000 ml of methylene chloride was added dropwise a cooled ( $15^{\circ}$ ) solution of 188.0 g (2.65 mole) of chlorine in 3000 ml of methylene chloride. Time of addition was 2.5 hours. After 18 hours at room temperature, the reaction mixture was concentrated under rotary evaporation at  $25^{\circ}$  (30 mm Hg) to give 341.7 g of light liquid. Distillation gave 277.0 g (78%) of light yellow liquid, bp  $45-46^{\circ}$  (3 mm Hg); ir (methylene chloride): 3000-2800 (C-H), 1749, 1703 (C=O), and 1204-1024 (C-OC)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  0.94 (3H,  $\text{CH}_3$  of ethyl), 1.65 (2H,  $\text{CH}_2$ ), 1.33 (3H,  $\text{CH}_3$ ), and 5.08 (1H, CH).

#### Reaction of 1a with 2a. Preparation of 3a, 4, and 5.

Compound 2a (18.2 g, 0.145 mole) was added to a stirred solution of 23.0 g (0.097 mole) of 1a in 200 ml of chilled ( $-15^{\circ}$ ) methylene chloride. Then at that temperature, 18.7 g (0.145 mole) of diisopropylethylamine was added dropwise (5 hours) to the stirred mixture. The mixture was stirred at  $0-5^{\circ}$  for 14 hours, poured over 200 ml of ice water, and made slightly acidic with hydrochloric acid. The phases were separated. The organic phase was washed with water, dried (magnesium sulfate), and the solvent evaporated. The residue was chromatographed over a column of silica gel, using methylene chloride as eluent. Three fractions were collected.

The first fraction consisted of 5.7 g (18%) of crystalline solid 3a, mp  $95-97^{\circ}$ ; gc-ms: m/z 330 ( $\text{M}^+$ ), 315 ( $\text{M}^+\text{CH}_3$ ), 303 ( $\text{M}^+\text{HCN}$ ), 271 ( $\text{M}^+\text{CO}_2\text{CH}_3$ ), 245 ( $\text{M}^+\text{CO}_2\text{CH}_2\text{CN}$ ), 239 ( $\text{M}^+\text{SCO}_2\text{CH}_3$ ), 225, 212 (m/z 239-HCN), 198, 176, 172, 68 ( $(\text{CH}_3)_2\text{CHCN}^+$ ), 59 ( $\text{CO}_2\text{CH}_3$ ); ir (potassium bromide): 3354 ( $^1\text{NH}$ ), 3000-2800 ( $^1\text{CH}$ ), ca. 2200 (C=N), 1736 (C=O), and 1236-1150 (C-OC)  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.3 (3H,  $\text{CH}_3$  of  $\text{C}_2\text{H}_5$ ), 1.79 (6H,  $(\text{CH}_3)_2$ ), ca. 3.90 (5H,  $\text{OCH}_3$  and  $\text{CH}_2$ ), 5.6 (1H, NH).

The second fraction was characterized as the disulfide 4, 2.77 g (8.0%) of light amber syrup; ir (methylene chloride): 3420 (NH), 3000-2800 (C-H), 1738 and 1713 (C=O), 1570 and 1557 (C=N) and 1144 (C-OC)  $\text{cm}^{-1}$ ; gc-ms: m/z 362 ( $\text{M}^+$ ), 335 ( $\text{M}^+\text{HCN}$ ), 327 ( $\text{M}^+\text{HCl}$ ), 297 ( $\text{M}^+\text{HS}_2$ ), 242, 198, 176, 68 ( $\text{C}_3\text{H}_7\text{N}^+$ ), 64 ( $\text{S}_2^+$ ), 59 ( $\text{CH}_3\text{CO}_2^+$ ), 41.

Anal. Calcd. for  $\text{C}_{11}\text{H}_{15}\text{ClN}_6\text{O}_2\text{S}_2$  (362.84): C, 36.4; H, 4.2; S, 17.7. Found: C, 36.6; H, 4.3; S, 17.9.

The third fraction, 1.5 g, contained two major and three minor components. The predominant product was tentatively assigned structure 5. Relative abundance and assignments are as follows:

Peak	Area (% Total)	Assignment	( $\text{M}^+$ )
A	10	$(\text{CH}_3\text{OC}(\text{O})\text{S})_2$	182
B	1	1a	240
C	35	isomer of 3a	330
D	1	isomer of 3a	330
E	44	5	420
F	2	isomer of 5	387 ( $\text{M}^+\text{SH}$ )

#### Reaction of 1h with 2f. Preparation of 5.

To a stirred solution of 4.0 g (0.016 mole) of 1h in 60 ml of methylene chloride was added dropwise 3.5 g (0.021 mole) of 2f, followed by the dropwise addition, at ambient temperature, of 2.7 g (0.021 mole) of Hünig's base. After 2 hours, the reaction mixture was diluted with 75 ml of ice water, acidified with diluted hydrochloric acid, and phase-separated. The dried organic layer was concentrated and purified by silica chromatography to give 1.0 g (15%) of 6 as a yellow syrup; ir (methylene chloride): 3426 (NH), 3000-2800 (C-H), 1717 (C=O), 1600-1500 (triazine), 1200-1000 (C-OC)  $\text{cm}^{-1}$ ; ci-ms: m/z 421 ( $\text{MH}^+$ ); ei-ms: m/z 385 ( $\text{M}^+\text{Cl}$ ), 346 ( $\text{M}^+\text{C}_4\text{H}_9\text{OH}$ ), 319 ( $\text{M}^+\text{CO}_2\text{C}_4\text{H}_9$ ), 287 ( $\text{M}^+\text{SCO}_2\text{C}_4\text{H}_9$ ), 186, 108, 83, 57 ( $\text{C}_4\text{H}_9^+$ );  $^1\text{H}$  nmr (deuteriochloroform): ca. 0.90 (5H,  $\text{C}_3\text{H}_5$ ), ca. 1.6 (2H,  $\text{CH}_2$ ), 1.27 (3H,  $\text{CH}_3$ ), 1.76 (6H,  $(\text{CH}_3)_2$ ), 2.41 (3H,  $\text{CH}_3$ ), 2.71 (1H, CH), 4.93 (1H, OCH), 5.52 (1H, NH), and 5.81 (1H, NH).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{23}\text{Cl}_2\text{N}_2\text{O}_2\text{S}$  (420.36): C, 45.7; H, 5.5; N, 16.7. Found: C, 45.4; H, 5.9; N, 16.8.

Supplementary Material Available.

Complete X-ray data on compound (3a) are available upon request from the author (KHP) including tables of fractional atomic coordinates for non-hydrogen atoms, thermal parameters, bond lengths, bond angles, intermolecular contacts, mean planes, and torsion angles (20 pages).

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- [16] Texray is a registered trademark of Molecular Structure Corporation, 1985.
- [17] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.
- [18] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.
- [19] The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.