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The Crystal and Molecular Structure of Ethylene Thiocyanate

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The structure of NCS · H_2C-CH_2 · SCN has been determined from single-crystal X-ray data. The crystals belong to the space group, $D_{2h}^{15}-Pbca$, with four molecules in a unit cell of dimensions: $a = 7.39$ Å, $b = 7.81$ Å, $c = 11.48$ Å. The molecules have a centrosymmetric, *trans* form, with the cyanide groups rotated out of the SCCS plane.

The bond lengths and angles are: C—C = 1.51 ± 0.03 Å, C—S = 1.80 ± 0.01 Å, S—C = 1.63 ± 0.01 Å, C—N = 1.18 ± 0.02 Å, ∠C—C—S = 110.7 ± 0.9°, ∠C—S—C = 99.4 ± 0.7°. The results indicate that the thiocyanate group is a hybrid of the structures $\diagup S-C\equiv N$ and $\diagup \overset{+}{S}=C=\overline{N}$. A value of 172° was found for the S—C—N angle, but the deviation from linearity is probably not significant.

In the course of preliminary work on the crystal structure of sulphur dithiocyanate [1], one of the present authors became interested in the nature of bonding in the thiocyanate group and its configuration and dimensions in other covalent compounds. Ethylene thiocyanate, NCS · H_2C—CH_2 · SCN, was chosen for study because of its simple formula and since the molecules, from literature data on other symmetrically disubstituted ethanes, might be expected to lie in crystallographic centres of symmetry.

CRYSTAL DATA

Ethylene thiocyanate (1,2-dithiocyanato-ethane) was prepared from ethylene bromide by heating in ethanol solution with a slight excess of potassium thiocyanate [2]. The compound melts at 90°C and vaporizes slowly in open air at room temperature. From chloroform, it crystallized as orthorhombic plates {010}, or as bipyramids {111} with in most cases {010} more or less developed. Buff [2], in 1856, described it as crystallizing from ethanol in rhombic plates.

From Weissenberg photographs, the axial lengths are: $a = 7.39$ Å, $b = 7.81$ Å, $c = 11.48$ Å. They are based on $\lambda(CuK_\alpha) = 1.542$ Å and are

believed to be accurate to better than 0.5 %. There are four molecules per unit cell; density, calc. 1.45, found 1.42 g/cm^3. The space group, from systematic absences, is D_{2h}^{15}—*Pbca*, which has eightfold general positions, and fourfold sets of symmetry centres as special positions. It follows that the molecules are centrosymmetric in the crystals.

The intensities of the 0*kl* and *h*0*l* reflections were estimated visually from Weissenberg photographs, taken with CuK_α radiation for which the absorption coefficient of the crystals is 63.2 cm^{-1}. Crystals with small, nearly uniform diameters were used in order to minimize absorption and spot shape effects. Out of 58 possible 0*kl* reflections within the range sin $\Theta < 0.985$ (CuK_α radiation) 53 were recorded with measurable intensity, the corresponding figures for *h*0*l* being 50 out of 59. The intensities were corrected in the usual way to give sets of relative structure amplitudes; these were eventually put to an approximately absolute scale by comparison with the calculated values.

The latter were based on the atomic scattering curves of Viervoll and Ögrim [3] for sulphur and hydrogen, and of Berghuis *et al.*[4] for nitrogen and carbon.

All summations were performed by means of Beevers-Lipson strips, at 6° intervals.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

There is one sulphur, one nitrogen and two carbon atoms in the asymmetric unit, apart from two hydrogen atoms, and conditions should thus be favourable for use of the heavy atom method in the initial stages.

From the *a*-axis Patterson projection, the coordinates, $y = 0.02$, $z = 0.075$ were derived for sulphur. A F_o synthesis based on 35 of the largest 0*kl* terms, with signs corresponding to the sulphur contributions alone, gave an electron density map where the general outline of the molecule could be recognized, but extensive overlapping occurred and further work on this projection was postponed until use could be made of *z* coordinates obtained from the *h*0*l* data.

The *b*-axis Patterson projection gave $x = 0.25$, $z = 0.078$ for sulphur, and these coordinates were used to derive the signs of 42 of the largest *h*0*l* terms for a subsequent F_o synthesis. Although overlapping of atoms was evident also here, the electron density map, together with considerations of probable bond lengths and the assumption of a linear thiocyanate group, allowed approximate coordinates for the nitrogen and carbon atoms to be determined. Signs were then calculated for all observed *h*0*l* structure factors, and none of these signs changed later. The electron density map thus obtained is shown in Fig. 1.

The refinement of this projection proceeded as follows. With $x = 0.25$, the sulphur atom lies in or close to the glide plane *b* at $x = \frac{1}{4}$, and overlaps with another sulphur atom belonging to a different molecule. The shape of the composite peak indicated that the sulphur atom should be slightly removed from the glide plane, and on changing *x* from 0.25 to 0.26 and then to 0.267 the reliability index *R* (using at this stage an overall, isotropic temperature correction with $B = 5.0$ Å^2) dropped from 0.135 over 0.123 to 0.115. Small adjustments in the nitrogen and carbon coordinates led to a further improve-

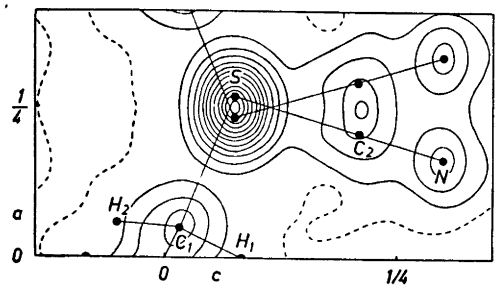

Fig. 1. Electron density projection of ethylene thiocyanate along the *b* axis. The 1-electron line is dashed, and the first full contour line is at 3 e · Å^{-2}. Intervals thereafter: 3 e · Å^{-2} for the sulphur atom and 2 e · Å^{-2} for the nitrogen and carbon atoms. The final atomic positions are marked with dots.

ment in R of about 0.01; from then on, refinement was carried out by means of (F_o—F_c) syntheses. In the first difference map, peaks appeared which were taken to indicate the positions of the two hydrogen atoms. When the hydrogen contributions were included in the calculated structure factors, with hydrogen coordinates chosen within the peaks on the basis of C—H = 1.1 Å and tetrahedral carbon, the value of R dropped by 0.02 to 0.085. Five more difference refinements were made.

Work on the *a*-axis projection was then resumed. The *z* coordinates were here, until after the fourth difference synthesis, kept equal to those found from the *h0l* data. Trial calculations on *y* coordinates relatively soon led to the determination of the correct signs of all observed *0kl* structure factors; the corresponding electron density map is shown in Fig. 2. The reliability index, using $B = 5.0$ Å^2 in the temperature factor as above, was at this stage 0.20. By trial and error, this figure was reduced to 0.13. At that stage the hydrogen contributions were included, based on the same *z* coordinates as in the *b*-projection and *y* coordinates derived by taking C—H = 1.1 Å. R then dropped to 0.115. Finally, extensive (F_o—F_c) refinement was carried out.

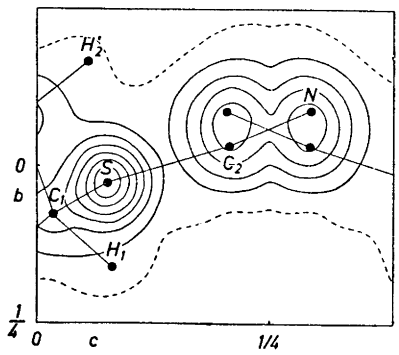

Fig. 2. Electron density projection along the *a* axis. All full contour lines are at intervals of 3 e · Å^{-2}, otherwise as in Fig. 1.

In both projections the difference maps indicated individual and partly anisotropic temperature corrections. In the temperature factor $\exp[-B(\sin^2\Theta/\lambda^2)]$ finally chosen the values of B were: For the $h0l$ data, $B = 4.6$ Å^2 and 5.5 Å^2 for the carbon atoms C_1 and C_2, respectively, 5.2 Å^2 for the nitrogen atom and $(4.3 + 0.4 \cos^2 \varphi)$ Å^2 for the sulphur atom, where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom, the a axis. For the $0kl$ data, $B = 5.0$ Å^2 for C_1 and 5.7 Å^2 for C_2, and $(5.2 + 1.2 \cos^2 \varphi)$ Å^2 and $(4.5 + 1.2 \cos^2 \varphi)$ Å^2 for the nitrogen and the sulphur atom, respectively. Here, the direction of maximum vibration was for both atoms taken to be that of the b axis, although in the case of sulphur a slightly different direction was indicated in the last maps. For the hydrogen atoms, $B = 5.0$ Å^2 in both zones. The large thermal parameters are in agreement with the relatively low melting point and high sublimation pressure of the substance.

The final atomic coordinates are given in Table 1. Two independent sets of z coordinates were obtained, namely, $z(S) = 0.0770$ and 0.0765, $z(N)=0.299$ and 0.297, $z(C_1) = 0.016$ and 0.017, $z(C_2) = 0.208$ and 0.206, from the $h0l$ and $0kl$ data, respectively. The mean values are listed in the Table. The hydrogen coordinates, which of course are approximate only, are for H_1: $x = 0.056$, $y = 0.168$, $z = -0.056$, and for H_2: $x = -0.019$, $y = 0.155$, $z = 0.082$.

Table 1. Atomic coordinates, in fractions of corresponding cell edges. Origin at a centre of symmetry.

	x	y	z
S	0.268	0.027	0.0768
N	0.165	−0.088	0.298
C_1	0.051	0.080	0.016$_5$
C_2	0.205	−0.029	0.207

Observed and calculated $h0l$ and $0kl$ structure factors are listed in Table 2. The reliability index, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.047 for the $h0l$ data and

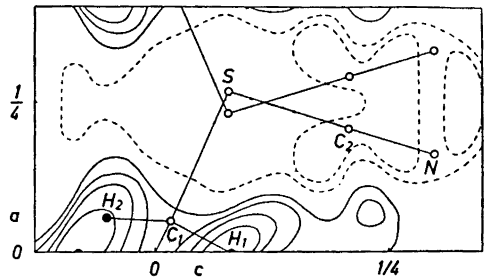

Fig. 3. Difference projection along the b axis, with hydrogen atoms *not* subtracted. Their positions are marked with dots, those of the other atoms with rings. Contour lines at −0.4, −0.2, 0.2, 0.4 ... e · Å^{-2}, with negative lines dashed.

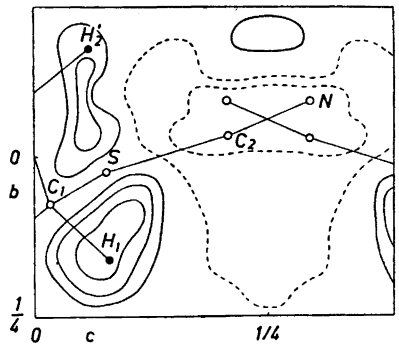

Fig. 4. Difference projection as in Fig. 3, along the *a* axis.

0.056 for the 0*kl* data. If the hydrogen contributions to F_c are omitted, the R values increase to 0.078 and 0.081, respectively. The effect is thus quite large. The difference maps of Figs. 3 and 4, calculated after ended refinement on the basis of F_c values with hydrogen contributions not included, are reproduced to show the hydrogen peaks and the assumed hydrogen positions.

The extent to which the projections could be refined was in the last stages felt to be limited by lack of accuracy of the experimental data. An estimate of random errors in the F_o, made by comparing values from different quadrants of a film, and scaled values from different films in the multiple-exposure series, led to reliability indexes of 2.5—3.0 % for the F_o for both zones.

ASSESSMENT OF ACCURACY

The standard deviation in electron density, evaluated as the root-mean-square of the figures in the difference maps, is slightly above 0.2 e · Å^{-2} for both zones, and the r.m.s. gradient of the difference maps is about 0.7 e · Å^{-3} in both axial directions of each map. The estimation of standard deviations in atomic coordinates on the basis of the gradients and the curvatures of the electron density peaks [5,6] is rendered uncertain by the rather extensive overlapping which occurs in both projections. Use of the method on the relatively well resolved nitrogen atom in the *b*-axis projection gave $\sigma(x) = 0.013$ Å, $\sigma(z) = 0.010$ Å for this atom. Assuming that the errors are the same for all three coordinates of an atom, and that they are inversely proportional to the atomic number, one gets $\sigma = 0.005$ Å for the sulphur coordinates and 0.011—0.015 Å for the nitrogen and carbon coordinates. The figures are relatively large despite the good agreement between observed and calculated structure factors, owing to the large thermal vibrations of the atoms and correspondingly low curvature of the electron density peaks. Because of the overlapping, the errors may be considerably larger than should be expected from the calculated standard deviations; however, the correspondence between the two independently determined sets of z coordinates, one from each zone, indicates that the estimates are of a reasonable order of magnitude. The difference between the z coordinates is 0.006 Å for sulphur, 0.01 Å for C_1 and 0.02 Å for C_2 and N.

Table 2. Observed and calculated *h0l* and *0kl* structure factors for ethylene thiocyanate.

l	F_o	F_c
	h0l zone	
	00*l*	
2	34	+35
4	20	+21
6	38	−36
8	36	−37
10	17	+17
12	9	+10
14	12	+11
	10*l*	
2	78	−77
4	75	−75
6	13	−13
8	26	+24
10	21	+21
12	8	+ 8
14	7	− 6
	20*l*	
0	93	−99
2	16	+19
4	26	+24
6	51	+51
8	37	+36
10	7	− 7
12	7	− 9
14	9	− 9
	30*l*	
2	54	+55
4	36	+34
6	13	+12
8	26	−27
10	24	−21
12	8	− 8
14	<1	+ 2
	40*l*	
0	52	+49
2	33	+33
4	12	−11
6	29	−29
8	14	−14
10	<4	+ 2
12	10	+ 9
	50*l*	
2	37	−33
4	19	−19
6	15	−15
8	10	+10
10	8	+ 8
12	<2	+ 1
	60*l*	
0	16	−16
2	19	−21
4	6	+ 7
6	14	+15
8	5	+ 5
10	<3	+ 1
	70*l*	
2	11	+12
4	7	+ 8
6	<3	+ 2
8	7	− 7
	80*l*	
0	<3	+ 2
2	<3	+ 4
4	6	− 6
6	7	− 7
8	<1	− 3
	90*l*	
2	<2	− 3
4	3	− 4
	0kl zone	
	00*l*	
2	37	+35
4	23	+22
6	39	−36
8	39	−37
10	17	+16
12	7	+ 9
14	10	+11
	02*l*	
0	153	+153
1	27	+28
2	25	+20
3	60	−56
4	2	+ 3
5	15	−16
6	35	−33
7	6	+ 5
8	28	−28
9	3	− 3
10	9	+10
11	6	+ 7
12	8	+ 8
13	5	− 4
14	8	+ 8
	04*l*	
0	31	+31
1	6	+ 9
2	13	+13
3	45	−47
4	14	−14
5	18	−18
6	26	−26
7	5	+ 4
8	15	−15
9	<3	+ 2
10	<3	0
11	7	+ 8
12	6	+ 6
13	4	− 3
	06*l*	
0	3	+ 3
1	5	− 6
2	5	+ 4
3	23	−23
4	9	−11
5	10	−11
6	14	−14
7	3	+ 3
8	7	− 6
9	7	+ 7
10	2	− 2
11	5	+ 6
	08*l*	
0	<3	0
1	5	− 5
2	<3	0
3	10	−10
4	2	− 3
5	4	− 5
6	3	− 3
7	3	+ 2
8	<2	− 2
9	3	+ 5

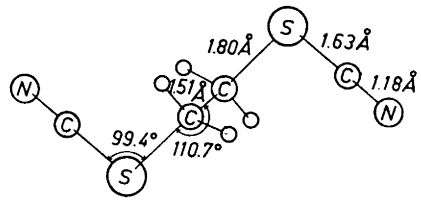

Fig. 5. The ethylene thiocyanate molecule as it appears in projection along the *b* axis.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The dimensions of the ethylene thiocyanate molecule were calculated from the coordinates of Table 1 and are listed in Table 3. A prime is used to denote the equivalent of an atom in the other half of the molecule across the centre of symmetry.

The ethane carbon and the sulphur valency angles are normal, and the lengths of bonds involving the ethane carbon atoms correspond within the errors to single bonds, as should be expected. In the thiocyanate group the value, 172.3 ± 1.3°, obtained for the S—C—N angle indicates that the group may not be linear. Least squares straight lines through the projected atoms, with the sulphur coordinates given three times the weight of the carbon and nitrogen coordinates, pass at shortest distances of 0.011 Å, 0.064 Å and 0.031 Å, respectively, from S, C and N in the *a*-projection, and at 0.002 Å, 0.012 Å and 0.007 Å in the *b*-projection. The largest deviation occurs for C in the *a*-projection, in which this atom is subject to heavy overlapping and may well have larger coordinate errors than corresponding to the e.s.d. of about 0.015 Å. Thus, the deviation from linearity of the thiocyanate group is probably not significant.

Table 3. Bond lengths and angles.

$C_1'-C_1 = 1.51 \pm 0.03$ Å	$\angle C_1'-C_1-S = 110.7 \pm 0.9°$
$C_1-S = 1.80 \pm 0.01$	$\angle C_1-S-C_2 = 99.4 \pm 0.7°$
$S-C_2 = 1.63 \pm 0.01$	$\angle S-C_2-N = 172.3 \pm 1.3°$
$C_2-N = 1.18 \pm 0.02$	

Some non-bonded distances within the molecule.

$C_1-C_2 = 2.61$ Å	$S-N = 2.80$ Å	$S-S' = 4.36$ Å
$C_1-N = 3.59$	$S-C_1' = 2.72$	$N-N' = 8.47$

The lengths found for the S—C and C—N bonds of the thiocyanate group, namely 1.63 ± 0.01 Å and 1.18 ± 0.02 Å respectively, can be interpreted in terms of the structures:

$$\diagup S-C\equiv N \qquad \text{and} \qquad \diagup \overset{+}{S}=C=\overline{N}$$

(I) (II)

The lengths of pure single, double and triple bonds are taken to be:

S—C = 1.78 Å	C=N = 1.26 Å
S=C = 1.59	C≡N = 1.16

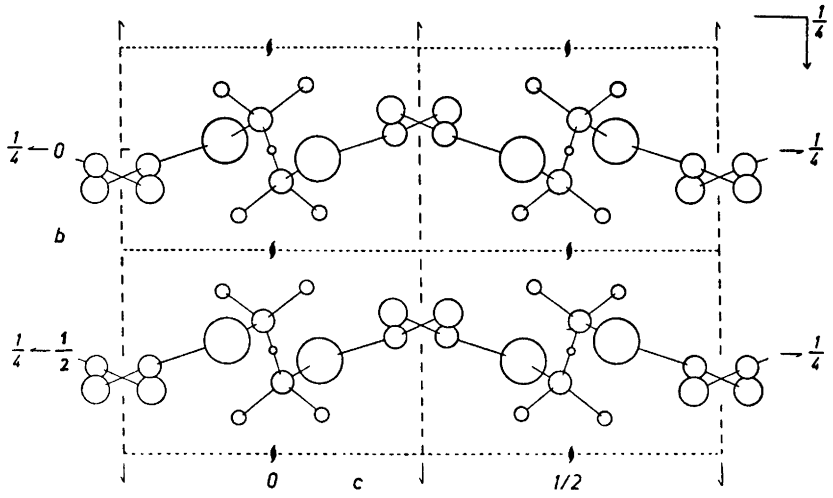

Fig. 6. The arrangement of molecules in the unit cell as seen along the *a* axis. In order of decreasing size the circles mark sulphur, nitrogen, carbon and hydrogen atoms.

In arriving at these figures, the single- and double-bond radii of carbon, 0.771 Å and 0.677 Å which are valid for sp^3 and sp^2 hybridization, respectively, of the carbon σ-bond orbitals, have been reduced by about 0.035 Å and 0.015 Å, respectively, to account for the *sp* state of hybridization of the carbon σ-bond orbitals in the thiocyanate group. The shortenings *cf.* [7,8] are based on evidence from C—H bonds with carbon in the appropriate valency states.

The found bond lengths indicate that structures I and II both contribute. The length of the thiocyanate group, *i. e.*, the S—N distance, is 2.80 Å whereas the calculated length is 2.94 Å for structure I and 2.85 Å for structure II. In view of the magnitude of the probable errors, and uncertainties in the bond order-bond length data, the results do hardly permit any conclusion beyond the one that structure II appears to be at least as important as structure I.

No structural data are available for other organic thiocyanates. Beard and Dailey [9] have made a microwave study of gaseous methyl thiocyanate, but did not determine the bond lengths. Assuming S—C = 1.61 Å and C—N=1.21 Å and a linear thiocyanate group, they arrived at 142° for the C—S—C angle, a value which appears unreasonable. Lindqvist's recent crystal structure determination of silver thiocyanate [10] led to S—C = 1.64 ± 0.03 Å and C—N = 1.19 ± 0.07 Å, and a not significant deviation from linearity of the thiocyanate group. The sulphur valency angle was here 180°, and also the nitrogen atom was covalently bonded to silver, so that the conditions are not quite comparable. The same applies to thiocyanic acid, which has the tautomeric structure H—NCS [11]. In the thiocyanate ion, from a crystal structure determination of the ammonium salt [12], the S—C and C—N bonds are 1.58 ± 0.02 Å and 1.24 ± 0.02 Å, and the ion linear. This corresponds to structure II above:

$S=C=\bar{N}$. More contribution of structure I is expected in a covalent thiocyanate, in agreement with the findings in ethylene thiocyanate.

The cyanogen halides, X—CN, are analogues of covalent thiocyanates in the respect that they contain a cyanide group linked to an atom with lone electron pairs. Particularly in the chloride, where X has nearly the same size as sulphur, conditions should be comparable, apart from the higher electronegativity of chlorine and thereby larger ionic character of the Cl—C bond relative to S—C. From microwave studies of the gases [13,14] the bond lengths in the linear cyanogen halide molecules are:

	ICN	BrCN	ClCN
X—C	1.995 Å	1.790 Å	1.630 Å
C—N	1.159	1.159	1.163

The C—N bond has in all three compounds close to triple-bond length, while the X—C bonds are about 0.1 Å shorter than single bonds. From nuclear quadropole coupling constants, estimates of the relative importance of structures corresponding to I and II were made for gaseous cyanogen iodide and bromide [15–17]. The data indicated 13 % contribution of II, X=C=N, in the iodide and 26 % in the bromide. In the chloride the percentage of II should be still higher, judging from the relative importance of $p\pi$-bonding from I, Br and Cl in aromatic compounds. Bonding conditions in the thiocyanate group thus appear to be about the same as in cyanogen chloride.

The ethylene thiocyanate molecule occurs in the *trans* configuration in the crystals, a molecular centre of symmetry being crystallographically required. This agrees with the finding from infrared measurements [18] that the compound exists in the *trans* form in the solid state, and with observations [19] that the stable form in the solid state of molecules of the types $X \cdot H_2C—CH_2 \cdot X$ and $X \cdot H_2C—CH_2 \cdot Y$ is, with few exceptions, the *trans* form. The cyanide groups are rotated out of the SCCS plane.

The arrangement of molecules in the unit cell as seen along the *a* axis is shown in Fig. 6. There are no particularly close intermolecular contacts.

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