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The Structure of Ethylenethiourea

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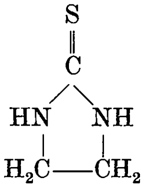
A detailed analysis has been made of the structure of ethylenethiourea (thioimidazolidone-(2)). The positions of the sulphur, nitrogen and carbon atoms were located by means of successive three-dimensional differential syntheses, and of the hydrogen atoms by a three-dimensional $(F_o - F_c)$ synthesis. The bond lengths show the occurrence of first-order conjugation between the non-bonding p electrons of the nitrogen atoms and the π electron system of the carbon/sulphur bond. There is no conclusive evidence from this analysis for the existence of hydrogen bonds between nitrogen and sulphur atoms, as several of the intermolecular distances are rather shorter than would be expected from a consideration of the van der Waals radii. Evidence is presented for believing that the molecule, which would be expected to be planar in isolation, is distorted slightly out of plane by the crystal forces. An examination is made of bond-length/bond-order curves for CN and CS obtained by both the molecular-orbital and resonance methods. It is concluded that the resonance method can, at present, provide a more useful and reliable basis for correlation and prediction of bond lengths in heteronuclear molecules than the molecular-orbital approach. A length of 1·59 Å is deduced for C=S.

Introduction

The specimen of ethylenethiourea (I) used in the present investigation was a commercial sample recrystallized from alcohol (m.p. 195° C.). It crystallizes in well-formed short needles conveniently elongated along either the a or the c axis, the predominating forms being either $\{010\}$, $\{100\}$ and $\{101\}$, or $\{010\}$, $\{001\}$ and $\{101\}$. The crystals are stable in air and exhibit no strong cleavage planes.



(I)

The unit-cell dimensions, measured from Straumanis photographs, are

$$a = 5{\cdot}774 \pm 0{\cdot}003,\ b = 14{\cdot}540 \pm 0{\cdot}005,$$
$$c = 5{\cdot}801 \pm 0{\cdot}003\ \text{Å},\ \beta = 101^\circ\ 18'\ .$$

The density determined by flotation is 1·45 g.cm.$^{-3}$ (calculated for four molecules in the unit cell, 1·42 g.cm.$^{-3}$). The systematic absences of ($h0l$) for h odd and ($0k0$) for k odd indicate unambiguously that the space group is $P2_1/a{-}C_{2h}^5$.

Weissenberg photographs were taken about the three principal axes, using Cu $K\alpha$ radiation. Different crystals were employed, all being considerably less than the optimum size ($\mu = 68{\cdot}7$ cm.$^{-1}$) in order to reduce absorption effects as far as possible. A multiple-film technique was used so as to embrace the necessary range of intensities. By these means a total of 1066 reflexions out of a possible 1130, observable with copper radiation, could have been observed, but 283 were either too weak to be seen or were absent for reasons of symmetry; this left a total of 783 independent planes on whose relative structure amplitudes the present investigation is based. The relative intensities of the reflexions were estimated visually by comparison with a standard chart, and each final intensity is the arithmetic mean of eight independent observations. The extension and compression of the recorded spectra of higher layer lines was allowed for as far as possible by ocular integration of the intensity. The strongest reflexions were obtained from the planes (040) and ($12\bar{1}$).

An optical examination in yellow light gave the following values for the principal refractive indices:

$$\alpha = 1{\cdot}64 \pm 0{\cdot}02,\ \beta = 1{\cdot}69 \pm 0{\cdot}01,\ \gamma = 1{\cdot}78 \pm 0{\cdot}03\ .$$

From the above data and from packing considerations some rough generalizations may be made about the structure. The strength of the (040) reflexion suggests that the four molecules in the unit cell are arranged side by side perpendicular to the b axis. The low birefringence and the absence of cleavage planes indicate that the planes of the molecules cannot be parallel. The approximate equality in length of the a and c axes, and the strength of the ($12\bar{1}$) reflexion give some indication of the angle of tilt of the molecule about the a and b axes.

There is one further piece of information which can be used to help in the elucidation of the structure. There are theoretical reasons for believing (see, for example, Coulson (1952)) that in cases of this kind the nitrogen atoms will be trigonally hybridized, and that first-order conjugation will take place between the non-bonding p electrons on the nitrogen atoms and the π electron system of the CS bond. Cox & Jeffrey (1951) have shown that there is a good deal of experimental evidence for this, and conclude that a nitrogen atom invariably has the trigonal valency state when it is adjacent to an unsaturated carbon atom. There is thus every reason to believe that the molecule is planar except for the methylene hydrogen atoms.

The X-ray structure analysis

The structure was first investigated in terms of projections, using Patterson F^2 projections on to planes normal to the a and c axes in order to obtain the coordinates of the sulphur atom. This was followed by Fourier F projections, using Bragg–Lipson charts to obtain the orientation of the molecule. The process of Fourier refinement was followed by (F_o-F_c) syntheses, which finally located the four hydrogen atoms attached to the carbon atoms. These four atoms were included in the ($hk0$) and ($0kl$) structure factors, and the final reliability factor for both projections was $R = 0{\cdot}09$. If the atoms are labelled as in (II), the coordinates given by the two projections are shown in Table 1, and the resulting bond lengths in Table 2.

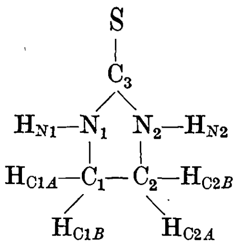
Table 1. *Atomic coordinates derived from projections expressed as fractions of the corresponding unit-cell dimension*

Atom	x	y	z
S	0·044	0·114	0·225
N_1	0·307	0·072	0·657
N_2	0·453	0·178	0·461
C_1	0·521	0·091	0·817
C_2	0·632	0·167	0·698
C_3	0·264	0·120	0·452

Table 2. *Bond lengths derived from projections*

Bond	Length (Å)
SC_3	1·642
C_3N_1	1·359
C_3N_2	1·372
C_1N_1	1·420
C_2N_2	1·558
C_1C_2	1·585

It will be seen that, despite the low value of R, there is a grave disparity in the lengths of chemically equivalent bonds.



(II)

The next stage in the analysis was the calculation of a set of structure factors for the general planes, and the computation of a three-dimensional differential synthesis on the Hollerith machines. The method described by Cox, Gross & Jeffrey (1949) was followed, except for minor alterations. The ($hk0$) and ($0kl$) structure factors had been calculated using the Hartree atomic scattering factors of the *International Tables*, with a temperature factor of $B = 3{\cdot}0$ Å^2. From the results of this differential synthesis, assuming that the peaks were spherically symmetrical, new atomic coordinates were found, corrected for termination-of-the-series effects, in the manner described by Booth (1948). A new set of (hkl) structure factors were obtained from these coordinates, and a plot of $\log (F_c/F_o)$ v. $\sin^2\theta/\lambda^2$ for different mean values of $\sin^2\theta/\lambda^2$ was drawn. A new temperature factor $B = 3{\cdot}7$ Å^2 was found from the slope of this graph, and this was applied to the Hartree scattering-factor curves published by Viervoll and Ögrim (1949). The structure factors were recalculated using these scattering factors, and gave a value of $R = 0{\cdot}17$. It was also found possible at a later stage to derive an experimental scattering curve for the sulphur atom from calculations on over 200 planes where more than 75 % of the structure factor was due to the scattering from the sulphur atom. It was found that the experimental curve deviated by an insignificant amount from the Hartree curve with a temperature factor of $B = 3{\cdot}7$ Å^2. Further, since no evidence of anisotropic thermal vibrations was ever obtained, this temperature factor was used for all atoms throughout the remainder of the analysis.

With the structure factors obtained from the new

Table 3. *Corrections and new atomic coordinates obtained from second differential synthesis*

(Fractional coordinates)

	Assumed	F_o	F_c	Corrected
Atom	x	x	x	x
S	0·044	−0·00034	+0·00020	0·0439
N_1	0·305	+0·00300	−0·00276	0·3052
N_2	0·455	−0·00003	+0·00073	0·4557
C_1	0·520	+0·00148	−0·00100	0·5205
C_2	0·630	−0·00209	+0·00098	0·6289
C_3	0·275	+0·00398	−0·00160	0·2774
	y	y	y	y
S	0·114	−0·00032	+0·00037	0·1141
N_1	0·068	−0·00046	−0·00080	0·0667
N_2	0·177	+0·00030	−0·00027	0·1770
C_1	0·090	+0·00061	−0·00051	0·0901
C_2	0·168	−0·00115	+0·00109	0·1679
C_3	0·120	−0·00041	−0·00007	0·1195
	z	z	z	z
S	0·225	+0·00078	−0·00024	0·2255
N_1	0·652	−0·00485	+0·00225	0·6494
N_2	0·468	+0·00416	−0·00189	0·4703
C_1	0·819	−0·00364	+0·00232	0·8177
C_2	0·696	+0·00086	−0·00225	0·6946
C_3	0·453	+0·00598	−0·00338	0·4556

The first column of figures refers to the assumed coordinates, the second and third to the corrections obtained from the observed and calculated syntheses respectively, and the fourth column to the corrected coordinates.

scattering curves, a second differential synthesis was evaluated on the electronic computer at Manchester University. From the resulting data the errors in the atomic coordinates were calculated without the assumption of spherical symmetry about the peak maxima. This involves (Booth, 1948) the computation of the off-diagonal second derivatives, but requires negligible additional time on an electronic computer. The maximum difference in an atomic coordinate or in a bond length occasioned by the assumption of spherical symmetry was 0·005 Å. The errors discovered by means of this differential synthesis, and the bond lengths derived from the corrected coordinates, are given in Tables 3 and 4 respectively.

Table 4. *Bond lengths derived from second differential synthesis*

Bond	Length (Å)
SC_3	1·703
C_3N_1	1·344
C_3N_2	1·316
C_1N_1	1·484
C_2N_2	1·462
C_1C_2	1·535

At this stage in the analysis the reliability factor had dropped to a value of $R = 0{\cdot}13$. Neither of the two pairs of chemically equivalent bonds, C_3N_1, C_3N_2 and C_1N_1, C_2N_2, showed a significant discrepancy from the mean values, 1·330 Å and 1·473 Å respectively, nor did the C_1–C_2 bond differ significantly from the accepted value of 1·54 Å for carbon/carbon single bonds. However, the differences of 0·028 Å and 0·022 Å between the lengths of the two pairs of carbon/nitrogen bonds were disappointingly large, and it was decided to carry the analysis a step further in the hope of reducing them, and also to discover the magnitude of the errors introduced by the neglect of the hydrogen atoms in a structure of this type.

Accordingly the hydrogen atoms were located by three-dimensional $(F_o - F_c)$ 'patch' syntheses, performed on the Hollerith machines in a manner similar to that described by Hodgson, Clews & Cochran (1948). The resulting coordinates are shown in Table 5.

Table 5. *Coordinates of the hydrogen atoms obtained from three-dimensional* $(F_o - F_c)$ *'patch' syntheses*

(Fractional coordinates)

Atom	x	y	z
H_{N1}	0·170	0·035	0·696
H_{N2}	0·451	0·224	0·349
H_{C1A}	0·618	0·033	0·826
H_{C1B}	0·467	0·117	0·930
H_{C2A}	0·754	0·148	0·649
H_{C2B}	0·617	0·222	0·758

A new set of structure factors was calculated using these coordinates for the hydrogen atoms, and the new set of heavy-atom coordinates listed in Table 3. A Hartree scattering curve was used for the hydrogen atoms, with the same temperature factor of $B = 3{\cdot}7$ Å^2 as was used for the remainder of the atoms. The reliability factor was reduced from 0·13 to 0·12 by the inclusion of the hydrogen atoms. It is also a matter of interest that no fewer than 711 of the 783 planes (i.e. 92%) had their phases decided by the sulphur atom. This figure is much higher than expected from a consideration of the relative importance of the sulphur atom, and is no doubt partly due to the proximity of the sulphur atom to the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes. However, if such a figure is general, there arises the possibility that the elucidation of similar structures might be accomplished by less lengthy methods.

Another differential synthesis was now computed, giving the corrections and final coordinates shown in Table 6. These coordinates, and the coordinates of the

Table 6. *Corrections and final atomic coordinates obtained from third differential synthesis*

(Fractional coordinates)

	Assumed	F_o	F_c	Corrected
Atom	x	x	x	x
S	0·044	−0·00035	+0·00030	0·0440
N_1	0·305	+0·00282	−0·00208	0·3057
N_2	0·456	−0·00082	+0·00066	0·4558
C_1	0·521	+0·00077	−0·00061	0·5212
C_2	0·629	−0·00105	+0·00081	0·6288
C_3	0·277	+0·00216	−0·00108	0·2781
	y	y	y	y
S	0·114	−0·00025	+0·00034	0·1141
N_1	0·067	+0·00053	−0·00012	0·0674
N_2	0·177	+0·00043	−0·00051	0·1769
C_1	0·090	+0·00062	−0·00077	0·0899
C_2	0·168	−0·00110	+0·00124	0·1681
C_3	0·120	−0·00074	−0·00139	0·1179
	z	z	z	z
S	0·226	−0·00023	+0·00033	0·2261
N_1	0·649	−0·00255	+0·00220	0·6487
N_2	0·470	+0·00227	−0·00105	0·4712
C_1	0·818	−0·00180	+0·00117	0·8174
C_2	0·695	+0·00237	−0·00240	0·6950
C_3	0·456	+0·00336	−0·00222	0·4571

The first column of figures refers to the assumed coordinates, the second and third to the corrections obtained from the observed and calculated syntheses respectively, and the fourth column to the final coordinates.

Table 7. *Dimensions of the ethylenethiourea molecule obtained from the coordinates given in Tables 5 and 6*

Bond	Length (Å)	Angle (°)	
SC_3	1·708	SC_3N_1	123·5
C_3N_1	1·315	SC_3N_2	126·2
C_3N_2	1·328	$N_1C_3N_2$	110·2
C_1N_1	1·480	$C_3N_1C_1$	112·8
C_2N_2	1·461	$C_3N_2C_2$	112·3
C_1C_2	1·536	$N_1C_1C_2$	103·0
N_1H_{N1}	1·00	$N_2C_2C_1$	101·8
N_2H_{N2}	0·98	$H_{C1A}C_1H_{C1B}$	128·3
C_1H_{C1A}	0·99	$H_{C2A}C_2H_{C2B}$	124·6
C_1H_{C1B}	0·87		
C_2H_{C2A}	0·87		
C_2H_{C2B}	0·87		

hydrogen atoms given in Table 5, yield the molecular dimensions shown in Table 7.

It will be seen from a comparison of Tables 3, 4, 6 and 7 that the introduction of the hydrogen atoms, together with some very small shifts in the heavier atoms, can make a difference of 0·023 Å in an atomic coordinate, and of 0·029 Å in a bond length. The largest corrections involved the atom C_3, and illustrate how important series-termination corrections can be, even at this late stage in a refinement.

The arrangement of the molecules in the unit cell is shown in Figs. 1 and 2. The closest distances of approach between the different pairs of atoms of adjacent molecules are $S \cdots S$ 4·20, $S \cdots C_1$ 3·47, $C_1 \cdots C_1$ 3·43, $N_1 \cdots N_1$ 3·66, $C_2 \cdots N_2$ 3·36 Å. Finally the two N atoms in any one molecule lie at a distance of 3·44 Å ($N_2 \cdots S$) and 3·48 Å ($N_1 \cdots S$) from S atoms in different molecules. The hydrogen atoms H_{N1} and H_{N2} each lie about 21° off the corresponding $N \cdots S$ lines.

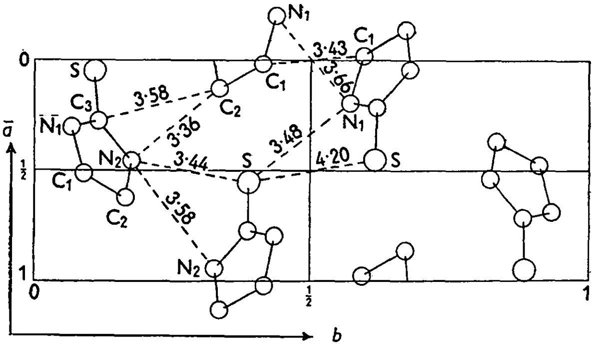


Fig. 1. Ethylenethiourea: projection on (001).

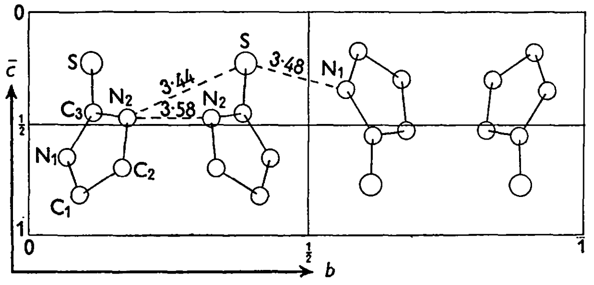


Fig. 2. Ethylenethiourea: projection on (100).

The accuracy of the analysis

A statistical survey of the accuracy of the analysis was made in the manner described in detail by Cruickshank (1949). The standard deviations of the slopes of the atomic peaks were calculated from formulae of the type

$$\sigma(A_x) = \frac{2\pi}{aV}\{\sum_G (\lambda m h \Delta F)^2\}^{\frac{1}{2}} ,$$

where $\sum_G$ denotes summation over all 'sub-sets', a 'sub-set' being defined as those members of a crystallographic form having the same value of $\cos(hx+ky+lz)$; λ is the r.m.s. value of $\cos(hx+ky+lz+\frac{1}{2}\pi)$; m is the number of reciprocal points in a sub-set; and $\Delta F = (F_o - F_c)$, (see Jeffrey & Rollett (1952), Cox, Gillott & Jeffrey (1949)). The mean values of the curvatures of the heavy atoms were taken from the figures obtained in the last differential synthesis, and the curvature of the hydrogen atoms estimated from the $(F_o - F_c)$ syntheses. The latter showed, as might be expected, a considerable scatter, and mean values were taken for the two types of hydrogen atoms, namely those attached to carbon and those attached to nitrogen atoms. The curvatures of the atomic peaks and the corresponding standard deviations of the atomic coordinates are shown in Table 8.

In the following discussion it will be assumed that the carbon and nitrogen atoms have a mean standard deviation of 0·008 Å in all directions, and that only a difference in a parameter greater than three times the standard deviation of that parameter (i.e. $\Delta/\sigma > 3{\cdot}09$) may be taken as real. With these assumptions it is found that the standard deviation of the mean of the bonds N_1C_1 and N_2C_2 is 0·008 Å, and hence the bonds may be considered equal ($\Delta/\sigma = 1{\cdot}2$) with a mean value of 1·471 Å. Similarly for C_3N_1 and C_3N_2 the standard deviation is 0·007 Å, and these bonds

Table 8. *Mean values of the curvatures, and the corresponding standard deviations of atomic coordinates*

	Mean value of the curvature (e.Å^{-5})				Standard deviation
Atom	F_o	F_c	$-(F_o-F_c)$	F_c/F_o	σ (Å)
S	−128·59	−131·42	−2·89	1·022	0·002
N_1	−30·42	−33·77	−3·35	1·110	0·008
N_2	−38·05	−39·10	−1·05	1·028	0·007
C_1	−30·00	−30·61	−0·61	1·020	0·008
C_2	−27·79	−30·09	−2·30	1·083	0·008
C_3	−37·17	−33·32	+3·85	0·896	0·007
H_C	− 8·62	—	—	—	0·064
H_N	−12·18	—	—	—	0·098

It will be seen in this table that, although the mean curvature of the H_N atoms is greater, the standard deviation is also greater. This is due to the much greater differences in the curvatures of the H_N atoms in the three principal directions. The standard deviations were obtained for each direction separately before the mean was taken.

may also be considered equal ($\Delta/\sigma = 0{\cdot}9$) with a mean length of 1·322 Å. Furthermore, the mean of the bonds C_1N_1 and C_2N_2 does not differ significantly from the accepted single-bond value of 1·48 Å ($\Delta/\sigma = 1{\cdot}1$), nor does the bond C_1–C_2 differ significantly from the single-bond value of 1·545 Å ($\Delta/\sigma = 0{\cdot}8$). However, the mean of the bonds C_3N_1 and C_3N_2 does differ significantly from the single-bond value ($\Delta/\sigma = 21{\cdot}9$) as well as from the double-bond value, which is not likely to be greater than 1·28 Å ($\Delta/\sigma = 6{\cdot}0$). In the same way the C_3S bond differs from both the single- and double-bond values, even though these are taken, respectively, at the extreme minimum and maximum of their permissible ranges.

The standard deviations of the angles were calculated from a formula due to Cruickshank & Robertson (1953). For all the angles relating heavy atoms, the standard deviation of the mean of chemically equivalent pairs is about 1°. For the angle $N_1C_3N_2$ the standard deviation is about 1·4°. It may be concluded, therefore, that the two members of pairs of chemically equivalent angles relating heavy atoms do not differ significantly from each other. The $N_1C_3N_2$ angle is 110·2°, and this differs significantly from 120° ($\Delta/\sigma = 7{\cdot}0$), which might be expected from the trigonally hybridized carbon atom, illustrating the strain in the ring. Similarly, the mean of the angles $N_1C_1C_2$ and $N_2C_2C_1$ differs significantly from the tetrahedral value ($\Delta/\sigma = 7{\cdot}1$), and the mean of the angles $C_3N_1C_1$ and $C_3N_2C_2$ differs from 120° ($\Delta/\sigma = 7{\cdot}6$), again illustrating the strain. The mean of the angles SC_3N_1 and SC_3N_2 also differs slightly from 120° ($\Delta/\sigma = 3{\cdot}5$), as would be expected from the low value of $N_1C_3N_2$. Another pair of angles that are of interest are $H_{C1A}C_1H_{C1B}$ and $H_{C2A}C_2H_{C2B}$. It will be seen from Table 7 that both these angles are found to be considerably greater than the tetrahedral value. Such an opening of the HCH angle is consistent with views of strain in a ring system. The standard deviation of these angles is, however, about 13°, so that, although it is tempting to believe that the increase is real, the present analysis cannot be regarded as convincing ($\Delta/\sigma = 1{\cdot}3$).

The large standard deviation attributable to the hydrogen atoms reduces any differences in C–H or N–H bond lengths into the insignificant range, even though these differences are large in an absolute sense. However, it is noticeable that all the C–H and N–H bond lengths are considerably shorter than those obtainable from, say, spectroscopic data. Indeed, for the three bonds C_1–H_{C1B}, C_2–H_{C2A} and C_2–H_{C2B} the usual test indicates that the difference from a normal bond (1·09 Å) is on the verge of significance ($\Delta/\sigma = 3{\cdot}06$). The fact that all six bonds involving hydrogen tend to be short is in agreement with previous work, and suggests that X-ray analysis will always yield small values for bonds involving hydrogen. This is understandable, of course, when it is remembered that X-rays are detecting the electrons rather than the nuclei, and that the displacement of the bonding electrons from the nucleus is proportionately greater for hydrogen than for any other atoms that are covalently bonded.

Taking account of all the factors discussed above, the molecular dimensions shown in Fig. 3 are considered to be most representative of the results of the analysis. The reliability of the different measurements vary, but all may be assessed quantitatively in terms of the standard deviations, using the significance level stated above.

The peak heights of the heavy atoms were determined during the evaluation of the differential syntheses, and the final values are shown in Table 9.

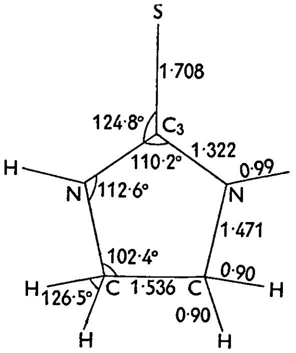


Fig. 3. Dimensions of the ethylenethiourea molecule.

Table 9. *Peak heights of the heavy atoms*

(Values in e.Å^{-3})

Atom	ϱ_o	ϱ_c	$(\varrho_o-\varrho_c)$	ϱ_c/ϱ_o
S	27·36	28·39	−1·03	1·038
N_1	7·79	8·54	−0·75	1·096
N_2	8·83	9·20	−0·37	1·042
C_1	7·11	7·35	−0·24	1·034
C_2	6·89	7·21	−0·32	1·046
C_3	8·02	7·57	+0·45	0·944

It will be noticed in Table 9, as well as in Table 8, how closely the values obtained from the observed and calculated structure factors follow each other. It will also be seen how closely the figures in Table 9 follow those in Table 8. To draw any conclusions from Table 9 it is necessary to know the standard deviation of the electron density. This was calculated from the formula

$$\sigma(\varrho) = \frac{1}{V}\{\sum_{3}(\Delta F)^2\}^{\frac{1}{2}}$$

and had the value

$$\sigma(\varrho) = 0{\cdot}17 \text{ e.Å}^{-3} .$$

This figure must be considered in relation to the third column in Table 9. It may be concluded that there is no significant difference between the peak heights of atoms N_1 and N_2 ($\Delta/\sigma = 2{\cdot}2$), nor between C_1 and C_2 ($\Delta/\sigma = 0{\cdot}5$), but that C_3 is significantly higher than C_1 and C_2 ($\Delta/\sigma = 4{\cdot}1$ and 4·5, respectively). The fourth column in Table 9 shows that, for all the atoms except C_3, the calculated density is greater than the observed density. The close parallelism between this column and the corresponding column in Table 8 suggests that it is an error in scale factor, rather than in temperature factor, that is causing this discrepancy, since an alteration in the temperature factor would change the curvatures more than it would change the peak heights. The mean scale factor found by the statistical plot is confirmed by the fact that

$$\Sigma F_c \div \Sigma F_o = 1\cdot009 \,.$$

This indicates that individual scale factors should be applied to the separate atoms, and hence that the atoms carry different amounts of formal charge. The two atoms that might be expected to be electrically neutral are C_1 and C_2, and it is interesting that, relative to these atoms, C_3 carries additional negative charge, whereas N_1 and N_2 are deficient in electrons. The slight indications from Tables 8 and 9 that the sulphur atom also has an additional negative charge is probably not real, since the experimental scattering curve for the sulphur atom agreed so closely with the Hartree curve. The qualitative conclusions regarding the disposition of charges within the molecule are in general agreement with the results expected if the nitrogen atoms are trigonally hybridized.

The peak heights of the hydrogen atoms obtained from the (F_o-F_c) syntheses are shown in Table 10.

Table 10. *Peak heights of the hydrogen atoms*

(Values in e.Å^{-3})

Atom	$(\varrho_o-\varrho_c)$
H_{C1A}	0·63
H_{C1B}	0·86
H_{C2A}	0·79
H_{C2B}	0·60
H_{N1}	0·42
H_{N2}	0·46

It will be seen that the heights of the two H_N atoms is considerably less than those of the four H_C atoms. Indeed, when the usual significance test is applied, the former are only probably significant ($\Delta/\sigma = 2\cdot7$ and $2\cdot5$). This is no doubt the reason why these two atoms were so difficult to locate in projection, and is probably due to greater thermal motion.

The planarity of the molecule

As a check on the planarity of the molecule, the equation of the best plane through the six heavy atoms of the molecule was obtained, and the perpendicular distances from this plane of these six atoms calculated. The results are shown in Table 11, together with the corresponding distances for H_{N1} and H_{N2}. The values for (Δ/σ) for the atoms are also listed. It will be seen that neither of the hydrogen atoms is significantly out of this plane. Indeed, at first sight it would appear that none of the atoms is significantly out of the plane. However, it will be noticed that three of the values of (Δ/σ) for the heavy atoms are probably significant, and, moreover, that there is a systematic variation in the atomic displacements. In order to test whether the systematic discrepancies of the heavy atoms from planarity is significant the 'χ^2' test was applied (Weatherburn, 1947). The values of $(\Delta/\sigma)^2$ were obtained, as shown in the third column of Table 11, yielding a value for

Table 11. *Distances of atoms from best plane through the molecule*

Atom	Distance (Å)	Δ/σ	$(\Delta/\sigma)^2$
S	$-0\cdot005$	2·5	6·3
N_1	$+0\cdot004$	0·5	0·3
N_2	$+0\cdot004$	0·5	0·3
C_1	$-0\cdot013$	1·6	2·6
C_2	$-0\cdot023$	2·9	8·4
C_3	$+0\cdot020$	2·5	6·3
H_{N1}	$-0\cdot069$	1·1	—
H_{N2}	$-0\cdot252$	2·6	—

$$\chi^2 = \Sigma\,(\Delta/\sigma)^2 = 24\cdot2 \,.$$

In the present application of the χ^2 test there are three degrees of freedom, since the equation for the plane applies three linear constraints. Tabulated values of χ^2 indicate that this value obtained for three degrees of freedom is highly significant, the probability of such a value occurring or being exceeded being about 0·0001. There can be only two reasons for this low probability. Either the molecule is not planar, or the estimates of the standard deviations are too low. Past experience shows that the values of the standard deviations of parameters obtained in the manner used in this paper are probably substantially correct, and are certainly not in error by the amount that would be demanded to bring this probability into the insignificant range. It can only be concluded, therefore, that the molecule is not strictly planar. There can be no question that, since the molecular environment is different on opposite sides, the molecule cannot be exactly planar, and the question then arises as to whether the departures from planarity indicated are reasonable in the light of the magnitude of intermolecular forces.

There is little doubt that the distortion of the molecule is made up in a complicated way by the sum of small effects at all the atoms. However, in order to discover whether any particular type of distortion was predominating, different selections of atoms were made, and the equations of the planes through these atoms obtained. The departures of the remaining atoms from these planes were then calculated. It was found that a satisfactory plane could be chosen only

Table 12. *Distances of atoms from the best plane through the five ring atoms*

Atom	Distance (Å)	Δ/σ	$(\Delta/\sigma)^2$
N_1	$-0\cdot001$	0·125	0·016
N_2	$-0\cdot001$	0·125	0·016
C_1	$+0\cdot003$	0·375	0·141
C_2	$-0\cdot003$	0·375	0·141
C_3	$+0\cdot001$	0·125	0·016

through the five ring atoms. The distances of the atoms from the best plane through the five ring atoms is shown in Table 12. These distances are very small, and the 'χ^2' test may be applied in order to discover whether they are significantly small. Proceeding as in the previous test, it is found that

$$\chi^2 = \Sigma(\Delta/\sigma)^2 = 0{\cdot}330\,.$$

The number of degrees of freedom is now two, and the tables of values of χ^2 show that the smallness of the sampling is not significant, the probability of obtaining a smaller value being about 0·15.

To a first approximation, therefore, the distortion can be described as a bending of the C=S bond out of the plane of the ring. The S atom is found to lie 0·030 Å from the best plane through the five ring atoms, a distance which is very significant (Δ/σ = 15·0). This distance corresponds to an angle of 1° between the S–C_3 bond and the plane of the ring. It has been shown by Linnett, Heath & Wheatley (1949) from a consideration of molecular vibrations, and by Linnett & Wheatley (1949) on wave-mechanical grounds that the bending of a π bond out of plane involves a reduction of the potential energy of the molecule, and hence that the efforts of the σ bond to retain planarity are partially offset by the increased overlap of the π orbitals. There is very little information available about the bending of the thione group, so that it is difficult to make quantitative calculations of the amount of energy involved. However, a rough estimate may be made of the relevant force constants. Linnett, Heath & Wheatley treated the formaldehyde molecule, and obtained the following values for the σ-bond and π-bond bending force constants

$$\begin{aligned} k_\sigma &= 1{\cdot}26\times10^{-11}\ \text{ergs/radian}^2\,,\\ k_\pi &= -0{\cdot}88\times10^{-11}\ \text{ergs/radian}^2\,. \end{aligned}$$

In the present case it seems reasonable to accept values of 0·8 and $-0{\cdot}2\times10^{-11}$ ergs/radian^2 for k_σ and k_π respectively, since a sulphur atom rather than an oxygen atom is involved, and there is evidently not a pure double bond between C_3 and S. The force constant opposing bending is thus $0{\cdot}6\times10^{-11}$ ergs/radian^2. The amount of energy involved in bending the S atom 1° out of the plane of the ring will therefore be

$$\sim\frac{1}{2}\times\frac{0{\cdot}6\times10^{-11}}{(57{\cdot}3)^2}\times\frac{6{\cdot}02\times10^{23}}{4{\cdot}18\times10^{7}}\ \text{cal./mole}\,,$$

$$\sim 13\ \text{cal./mole}\,.$$

Such a calculation as this must necessarily be very crude owing to the assumptions regarding the magnitude of the force constants and the nature of the potential function, but it is undoubtedly correct to within a power of ten. The important point is that the energy involved is very small compared with the 10–20 kcal./mole expected for the lattice energy, and suggests that distortions by crystal forces of molecules placed in unsymmetrical surroundings should be quite common. Indeed, the question arises as to why such distortions have not been detected before, and the answer probably lies in any or all of the following reasons:

(*a*) The statistical method of analysing results has rarely been applied.

(*b*) The effect is likely to be smaller in closed ring or fully conjugated ring systems, and the majority of organic molecules that have been investigated in detail are of this type.

(*c*) Provided the refinement is carried far enough, the effect is more likely to be discovered in a molecule containing, say, a thione rather than a ketone group, because of the smaller standard deviation of the sulphur atom.

(*d*) Ethylenethiourea is particularly susceptible to accurate analysis because its properties are much the same in all directions, thus dispensing with the need for introducing anisotropic temperature factors. Moreover, in the experimental work, the crystals are convenient to manipulate, and lend themselves to accurate intensity determination.

To sum up, therefore, it may be concluded that there is no evidence to suggest that the atoms H_{N1} and H_{N2} are not in the plane of the ring, but that there is evidence that the six heavy atoms do not all lie in one plane. There are probably small distortions at all the atoms, but the predominating effect seems to be that the sulphur atom lies out of the plane containing the five ring atoms.

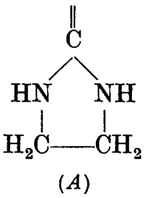
Discussion of the structure of ethylenethiourea

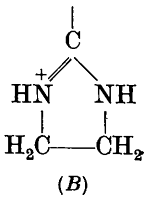
The melting point of ethylenethiourea (195° C.) is rather high; if the two NH groups are replaced by S atoms, the melting point drops to 36° C. (Challenger, Mason, Holdsworth & Emmott (1952)). The existence of hydrogen bonds between the nitrogen and sulphur atoms might account for this, and it may be seen from Figs. 1 and 2 that the nitrogen and sulphur atoms do lie slightly closer than would be expected from the sum of the van der Waals radii. Furthermore the H_N atoms are not far from the line joining the corresponding nitrogen and sulphur atoms. However, it will be seen that there are other intermolecular distances that are abnormally short, compared with the sum of the corresponding van der Waals radii, so that it must be concluded that there is no real evidence from this analysis for the presence of hydrogen bonds between nitrogen and sulphur atoms. It is more probable that the closeness of packing is due to direct electrostatic attraction between the formal charges on the different atoms.

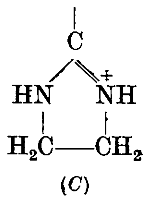
The bonds C_1N_1, C_2N_2 and C_1C_2 have lengths equal, within the experimental error, to the corresponding single-bond values. The bonds C_3N_1 and C_3N_2 have a mean length of 1·322 Å. The SC_3 bond length is 1·708 Å. From these figures it should be possible to deduce the length of C=S, which is at present uncertain. Such a deduction involves the assumption that unique order/length curves for pairs of atoms do, in fact, exist, and hence that second-order effects such as polarity of bonds, strain in rings, and environmental factors can be neglected; it also necessitates a choice, which must to some extent be arbitrary, between the different methods of assessing bond orders, two of which will be considered here.

Cox & Jeffrey (1951) determined the trend of the length/order curve for nitrogen and carbon by taking an interpolated value of 1·28 Å for C=N and by applying Coulson's (1939) molecular-orbital definition of bond order to Pauling & Sturdivant's (1937) value for the resonance energy of melamine, choosing this substance because of the near-equality of all the bonds and also because of the accuracy of their measurement (Hughes, 1941). However, the bond order of 1·66 obtained in this way seems to be too high, since it is unlikely that the total bond order of the three bonds around a carbon atom in melamine (i.e. $3\times1{\cdot}66=4{\cdot}98$) could be greater than, say, the value of 4·63 found for the central carbon atoms in naphthalene (Coulson, Daudel & Robertson, 1951). Moreover, these order/length curves based on molecular-orbital calculations give rise to difficulties not only in interpreting other measurements of CN bonds (e.g. Carpenter & Donohue, 1950; Cochran, 1951; Broomhead, 1951), but also in accounting for the present result for the CS bond. Reference to the curve given by Cox & Jeffrey for CS bonds shows that a length of 1·708 Å corresponds to an order of 1·64. If to this figure is added 1·78, obtained from Cox & Jeffrey's curve, for each of the bonds C_3N_1 and C_3N_2, a bond number of 5·20 is obtained for the atom C_3, which is again much too high. If the molecular-orbital calculations for intermediate bonds are rejected, these difficulties can be largely accounted for by the uncertainty in the lengths of C=N and C=S. There seems to be no doubt that both the CN and CS curves need revision and that the molecular-orbital method, as applied to heteronuclear bonds, is not at present sufficiently developed to provide a sound basis for this revision. We therefore turn to the resonance method.

Vaughan & Donohue (1952) have shown that a large range of observed bond lengths can be correlated by the use of Pauling's equation (1940), and a judicious choice of lengths for single and double bonds. If it is assumed that resonance occurs between the following structures in ethylenethiourea and if the values of 1·48 Å for C−N and 1·24 Å for C=N are accepted, as suggested by Vaughan and Donohue, it is found that *A*, *B* and *C* contribute 22%, 39% and 39% respectively. In other words the bond SC_3 has about 20% double bond character. If this figure of 1·22 for the order of the SC_3 bond is substituted in Pauling's equation, together with the value of 1·81 Å for C−S, a value of 1·59 Å is obtained for C=S. This is approximately the value indicated indirectly by other evidence (Cox, Gillott & Jeffrey, 1949), and it differs from the length of the CS bond in CS_2 by almost exactly the same amount as Vaughan and Donohue's value of 1·20 Å for C=O differs from the length of the CO bond in CO_2. Furthermore, if all the bonds in melamine are assumed equal with one-third double-bond character, Pauling's equation yields the value 1·346 Å for the length of the bonds, agreeing exactly with the mean value obtained by Hughes. Little faith can be placed in this exact agreement, of course, but it may be concluded that the resonance method does at least lead to a consistent set of values for the lengths and orders of bonds between C and O, C and N, and C and S atoms.


(*A*)


(*B*)


(*C*)

In a recent paper by Dewar & Longuet-Higgins (1952) the undoubted success of the resonance method has been explained by showing that a correspondence exists between the simple addition of canonical forms and the contribution from each of the occupied molecular orbitals. This relation between the resonance and molecular-orbital approaches suggests that, at the present time when molecular-orbital calculations are yielding anomalous values for bond orders, the resonance method can be more usefully and reliably employed than the molecular-orbital method for correlating and predicting bond lengths in heteronuclear molecules.

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The Crystal and Molecular Structure of α-Isosparteine Monohydrate

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As a test of stereochemical formulae proposed by Marion & Leonard for the thermopsine–anagyrine family of C_{15} lupin alkaloids, the structure of α-isosparteine monohydrate, $C_{15}H_{26}N_2.H_2O$, has been determined. The space group is $C222_1$, $a = 20{\cdot}18$, $b = 10{\cdot}61$, $c = 6{\cdot}84$ Å, $Z = 4$. The four rings of the molecule have the 'chair' form with both outer rings *trans* to the methylene bridge that is common to the two inner rings. Bond lengths and angles have been measured. The water molecule of the monohydrate does not appear to be hydrogen bonded to the alkaloid molecule.

Introduction

The thermopsine–anagyrine stereochemical family of C_{15} lupin alkaloids comprises thermopsine and anagyrine with composition $C_{15}H_{20}N_2O$, lupanine, α-isolupanine, and two other (at present unknown) isomers having the composition $C_{15}H_{24}N_2O$, and sparteine, α-isosparteine, and β-isosparteine of composition $C_{15}H_{26}N_2$ (Marion & Leonard, 1951). A provisional stereochemical structure was assigned to sparteine by Leonard & Beyler in 1950. Structures for the other members of the family have recently been proposed by Marion & Leonard (1951) on the basis of that for sparteine and a study of the course of catalytic hydrogenation reactions, with the aid of Fisher–Hirschfelder–Taylor scale molecular models. The family relationships are shown in Fig. 1, where *cis* and *trans* refer to the hydrogen atoms on C_6 and C_{11} relative to the $C_{7,9}$-methylene bridge, and the black discs represent these hydrogen atoms when in *cis* position. The lettering (*A*, *B*, *C*, *D*) of the four rings and the numbering of the C and N atoms are those of Marion & Leonard (1951). The principal assumption made in the identification of the various isomers with the possible stereochemical formulae was that, in accordance with the spatial configurations of the scale molecular models, hydrogen enters the $C_{15}H_{20}N_2O$ molecule at C_6 *cis* to the methylene bridge more readily than *trans*. The validity of this assumption can be tested by a detailed X-ray structure study of almost any one of the substances concerned.

With this object in view, it seemed desirable to select a completely hydrogenated member of the family to avoid possible complications due to double bonds and carbonyl groups. Of the three compounds fulfilling this condition, sparteine (*cis–trans*) obviously is the least suitable structurally, while β-isosparteine had not been characterized chemically when the present investigation was undertaken. The structure of α-isosparteine, however, if established as *cis–cis*, would immediately confirm that of its chemical progenitor, thermopsine, as blank-*cis* and thus indirectly those of the other isomers as represented in Fig. 1. This

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