The Experimental Charge Distribution in Sulfur-Containing Molecules. Structure Determination and Electron Density Study of NaSCN at Reduced Temperatures*

By J. W. Bats,† P. Coppens and Å. Kvick‡

Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214, USA
and Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York 11973, USA

The crystal structure of NaSCN (sodium thiocyanate) has been determined by X-ray diffraction studies at 150 and 81 K and a neutron diffraction study at about 94 K. The space group of the structure is *Pmcn*, the molecules being arranged in the mirror planes. The SCN group is approximately linear with CS and CN bond lengths of 1·647 (1) and 1·178 (1) Å respectively. Deformation density maps calculated from the 150 K and 81 K X-ray data are very similar. The deformation density around the C and N atoms suggests *sp*-hybridization, while the S lone-pair electrons are found in a diffuse ring around the S atom perpendicular to the C—S bond, indicating an almost unhybridized S atom. A charge-population analysis assigns a net charge of +0·27 (6) e to the Na atom.

Introduction

In the framework of the determination of the electron density distribution in compounds small enough to allow for comparison with theoretical studies, the crystal structure of $NaCN.2H_2O$ has recently been refined at 150 K (Bats, 1977). The present work is a similar low-temperature study of NaSCN.

After completion of this work a room-temperature analysis of NaSCN was reported by Van Rooyen & Boeyens (1975). In the present study two sets of X-ray data were used. The first was collected at 150 K with a gas-flow system, while the second set was from a dif-

ferent crystal mounted in a cryostat and cooled to 81 K. In addition, neutron data were collected. A temperature of 81 K was recorded during the neutron diffraction experiment, but comparison of the thermal parameters from the neutron and X-ray refinements suggest that the actual crystal temperature may have been about 94 K. The discrepancy is attributed to insufficient heat conduction between the crystal and the cryostat.

The following paper deals with an X-ray and neutron determination of the electron density distribution in NH_4SCN.

Experimental

Single crystals of NaSCN were easily grown from a solution in methanol, but had to be handled with care as they are very deliquescent.

Table 1. *General information*

	X-ray 150 K	X-ray 81 K	Neutron 94 K
a	4·047 (1) Å	4·038 (1) Å	4·035 (2) Å
b	5·604 (1)	5·602 (2)	5·601 (2)
c	13·279 (2)	13·281 (4)	13·276 (5)
V	301·18 (10) Å³	300·40 (16) Å³	300·04 (22) Å³
Space group	*Pmcn*	*Pmcn*	*Pmcn*
Z	4	4	4
Wavelength	0·71069 Å	0·71069 Å	1·0164 Å
$(\sin \theta/\lambda)_{max}$	1·10 Å⁻¹	1·22 Å⁻¹	0·70 Å⁻¹
Number of reflections	4182	3658	1294
Unique reflections	1822	1499	469
Crystal volume	0·031 mm³	0·017 mm³	5·00 mm³
μ	8·76 cm⁻¹	8·84 cm⁻¹	0·02 cm⁻¹
Transmission range	0·754–0·812	0·770–0·799	0·997–0·998

All crystals used for data collection were parallelepipeds showing the forms {1̄10} and {001}.

X-ray experiment 150 K

A crystal, 0·33 × 0·27 × 0·34 mm, was selected and sealed in a glass capillary. The crystal was kept at a temperature of 150 K using a flow of cold nitrogen gas. Crystallographic information is reported in Table 1.

Data were collected in three octants of reciprocal space up to sin θ/λ values of 1·10, 1·10 and 0·80 Å⁻¹, respectively, on a Picker FACS-I diffractometer using Nb-filtered Mo Kα radiation. Ice formation on the capillary slightly affected the intensities, but was minimized by interrupting the gas flow to allow the ice to melt whenever necessary.

Three standard reflections were measured after every 40 reflections and the data rescaled with respect to these standards. Except for a sudden increase in intensity of about 5% at the start of the second octant, no fluctuations of the standards of more than 2% were observed. The step-scan data were analyzed with the profile analysis described by Blessing, Coppens & Becker (1974). Lorentz, polarization and absorption corrections were applied, while deviations from counter linearity were corrected by the method of Chipman (1969). Averaging of symmetry-related reflections (Σ |F² − ⟨F²⟩|/Σ F² = 2·3%) resulted in 1712 independent reflections with F² > 0.

Weights were assigned to the averaged reflections according to w(F²) = [σ(F²)₍counting₎ + (kF²)]⁻², where σ(F²)₍counting₎ represents the standard deviation of an averaged reflection, determined from the counting statistics only. The proportionality factor k = 0·02 was estimated from discrepancies between symmetry-related reflections.

X-ray experiment 81 K

A crystal, 0·25 × 0·24 × 0·27 mm, was sealed in a glass capillary and mounted in the cryostat described by Coppens, Ross, Blessing, Cooper, Larsen, Leipoldt, Rees & Leonard (1974).

Data were collected at 81 K as described above in three octants of reciprocal space up to sin θ/λ values of 1·00, 1·00 and 0·75 Å⁻¹ respectively. In addition, 175 reflections in the range 1·00 < sin θ/λ < 1·22 Å⁻¹, which were calculated as having intensities above a measurable threshold value, were measured twice.

The intensities of three standard reflections measured after every 45 reflections fluctuated less than 1%.

Data were processed as described above. Symmetry-related reflections were averaged (Σ |F² − ⟨F²⟩|/Σ F² = 1·5%), resulting in 1458 independent reflections with F² > 0.

Weights were assigned to the averaged reflections according to: w(F²) = [σ²(F²)₍counting₎ + (0·015F²)² + 10²]⁻¹.

Neutron experiment 94 K

The neutron diffraction experiment was performed at the high-flux beam reactor of Brookhaven National Laboratory. A crystal, 1·6 × 2·9 × 1·0 mm, was glued on top of a quartz pin mounted in a liquid-nitrogen-cooled cryostat. A thermocouple placed inside the cryostat recorded a constant temperature of 81·5 K during the experiment, but comparison of the X-ray and neutron temperature parameters after refinement suggests that the actual crystal temperature was about 94 K. This may result from insufficient heat conduction in the quartz pin. Cell constants are given in Table 1. Data were collected in two octants of reciprocal space up to a sin θ/λ value of 0·70 Å⁻¹ with a wavelength of 1·0164 Å.

Two standard reflections measured after every 50 reflections showed no significant fluctuations. Data were reduced as described above.

Examination of strong reflections indicated the presence of considerable anisotropic extinction; therefore only Friedel pairs of reflections were averaged. Weights were assigned to each reflection according to w(F²) = [σ(F²)₍counting₎ + 0·03F²]⁻².

Structure determination and refinement

X-ray data 150 K and 81 K

From the systematic extinctions the space group could be either Pmcn or P2₁cn. A Patterson synthesis of the 150 K data indicated a layered structure and gave the position of the S atom. Other atoms were found in a Fourier map based on the S phases. The structure was refined satisfactorily in the space group Pmcn, in which all atoms lie in layers with x = 0·25 and x = 0·75. We note in particular that the U₁₁ thermal parameters which describe the thermal motion perpendicular to the mirror plane are not unusually large.

Neutral-atom scattering factors were taken from International Tables for X-ray Crystallography (1974). For the S and Na atoms, anomalous dispersion factors of Cromer & Liberman (1970) were used.

A refinement including a type I isotropic extinction parameter (Becker & Coppens, 1974) indicated a mosaic spread of 12 seconds at 150 K and 57 seconds at 81 K.

A survey of full-data and high-order (sin θ/λ > 0·65 Å⁻¹) least-squares refinements is given in Table 2, while atomic parameters are reported in Table 3.* All refinements reported in this paper were based on F.

Neutron data 94 K

Starting values for the atomic parameters were taken from the X-ray refinement. Neutron scattering lengths used were: $b_S = 0.2847$, $b_{Na} = 0.351$, $b_C = 0.6626$ and $b_N = 0.920 \times 10^{-12}$ cm (Shull, 1971; Kvick, Koetzle, Thomas & Takusagawa, 1974).

The least-squares refinement as described by Becker & Coppens (1975) indicated severe and anisotropic extinction and gave principal components of the extinction tensor [according to Thornley & Nelmes (1974)] corresponding to mosaic spreads of 1·7, 2·9, and 5·5 seconds. A second refinement excluding the reflections most seriously affected by extinction did not lead to any change in thermal parameters, thus supporting the consistency of the extinction formalism.

Agreement indices and atomic parameters are listed in Tables 2 and 3 respectively.*

Discussion of the structure

Bond distances and angles are reported in Tables 4 and 5, while a stereoscopic view of the structure is shown in Fig. 1.

The almost linear SCN groups and the Na ions are arranged in layers at $x = 0.25$ and 0·75. The Na atom is coordinated by three S and three N atoms. The coordination of the S atom is almost tetrahedral, but the N atom shows a distortion from a tetrahedral coordina-

---

* See previous footnote.

Table 2. *Survey of least-squares refinement*

| | X-ray 150 K | | X-ray 81 K | | |
	Conventional	High order	Conventional	High order	Neutron 94 K
$(\sin \theta/\lambda)_{min}$ (Å^{-1})	0·00	0·65	0·00	0·65	0·00
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	1·10	1·10	1·22	1·22	0·70
Number of reflections	1712	1314	1458	1016	904
Number of variables	26	25	26	25	31
Scale factor	14·20 (3)	14·38 (5)	8·33 (1)	8·33 (1)	177·1 (4)
$R(F)$ (%)	3·4	5·3	2·0	1·9	2·1
$R_w(F)$ (%)	3·7	4·1	2·2	1·6	2·3
Goodness of fit*	1·86	1·56	1·73	1·03	0·92

* Defined as $[\Sigma \, w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$.

Table 3. *Positional and thermal parameters*

All values are multiplied by 10^5.

| | | X-ray 150 K | | X-ray 81 K | | |
		Conventional	High order	Conventional	High order	Neutron 94 K
S	y	11839 (3)	11847 (4)	12085 (3)	12090 (2)	12013 (13)
	z	18590 (1)	18591 (2)	18613 (1)	18613 (1)	18592 (6)
	U_{11}	2386 (10)	2395 (11)	1287 (6)	1275 (5)	1494 (37)
	U_{22}	1285 (7)	1313 (9)	710 (5)	716 (4)	818 (33)
	U_{33}	1404 (7)	1427 (9)	768 (5)	770 (4)	939 (31)
	U_{23}	−75 (5)	−66 (5)	−57 (4)	−46 (3)	−15 (26)
Na	y	−6195 (8)	−6196 (10)	−5956 (5)	−5958 (5)	−6051 (12)
	z	39253 (3)	39249 (4)	39264 (2)	39264 (2)	39263 (5)
	U_{11}	2168 (17)	2216 (19)	1207 (12)	1205 (9)	1282 (29)
	U_{22}	1852 (15)	1853 (17)	1038 (10)	1022 (8)	1141 (30)
	U_{33}	1472 (13)	1493 (15)	832 (9)	837 (7)	1025 (26)
	U_{23}	82 (11)	67 (11)	18 (8)	28 (6)	64 (22)
C	y	−12049 (13)	−12033 (14)	−11884 (10)	−11842 (8)	−11899 (6)
	z	11421 (5)	11440 (6)	11425 (4)	11430 (3)	11421 (2)
	U_{11}	1580 (24)	1660 (24)	930 (19)	989 (13)	1072 (17)
	U_{22}	1327 (23)	1294 (21)	813 (16)	758 (10)	854 (18)
	U_{33}	1384 (21)	1407 (20)	805 (15)	800 (10)	918 (15)
	U_{23}	59 (17)	−53 (16)	51 (15)	−39 (10)	−54 (11)
N	y	−29245 (14)	−29289 (16)	−29149 (10)	−29167 (8)	−29174 (5)
	z	6432 (5)	6426 (6)	6411 (4)	6402 (3)	6412 (2)
	U_{11}	2804 (33)	2912 (36)	1541 (23)	1609 (17)	1826 (16)
	U_{22}	1593 (24)	1558 (23)	929 (16)	897 (11)	1015 (16)
	U_{33}	1682 (23)	1681 (23)	980 (16)	964 (11)	1135 (13)
	U_{23}	−231 (19)	−289 (18)	−132 (14)	−182 (9)	−242 (9)

Table 4. *Bond lengths* (Å)

| | X-ray 150 K | | X-ray 81 K | | |
	Conventional	High order	Conventional	High order	Neutron 94 K
C—S	1·643 (1)	1·640 (1)	1·647 (1)	1·645 (1)	1·643 (1)
		[1·6461]*		[1·648]	[1·647]
C—N	1·170 (1)	1·174 (1)	1·174 (1)	1·178 (1)	1·174 (1)
		[1·178]		[1·180]	[1·177]
S—Na	2·896 (1)	2·896 (1)	2·894 (1)	2·894 (1)	2·891 (1)
S—Na'	2·924 (1)	2·924 (1)	2·923 (1)	2·923 (1)	2·925 (1)
N—Na	2·423 (1)	2·422 (1)	2·425 (1)	2·424 (1)	2·423 (1)
N—Na'	2·589 (1)	2·588 (1)	2·581 (1)	2·581 (1)	2·582 (1)

* Values in brackets include a correction for libration assuming a rigid-bond model for the SCN group.

tion, one of the three Na—N interactions being shorter and more closely parallel to the SCN axis than the other two.

The CN bond length of 1·178 Å is somewhat longer than a triple CN bond of 1·153 Å, while the C—S bond length of 1·647 Å is in between a single and a double C—S bond, indicating that the π-bonding is mostly localized in the former bond.

The dimensions of the SCN group agree well with those in NH$_4$SCN described in the following paper and are similar to values for a number of thiocyanates recently reviewed by Mokuolu & Speakman (1975).

Comparison of the X-ray results at 150 and 81 K shows the thermal motion of the atoms to be approximately linearly dependent on the absolute temperature, which suggests that low-frequency external vibrations (rigid-body motions for the SCN group) form the main part of the thermal motion.

The center of libration around the axes normal to the axis of the SCN ion is found in the C—S bond at a distance of approximately 0·53 Å from the C atom. This is not far from the center of mass of a free SCN group (which is at 0·62 Å from the C atom).

Analysis of the chemical bonding

Effect on the atomic parameters

Differences between atomic positions from the high-order and full-data X-ray refinements are given in Table 6. Discrepancies are only found for the C and N atoms which are shifted into the CN bonds in the conventional refinements by amounts of 0·002 and 0·003 Å, when compared with the high-order parameters.
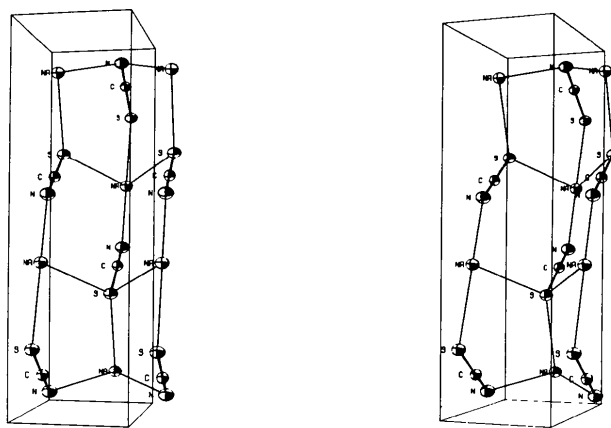

Fig. 1. Stereoscopic view of the structure (150 K). The thermal ellipsoids are the 50% probability surfaces.

Table 6. *X-ray asphericity shifts*
(*high order–conventional*) (Å ×10⁴)

	150 K	81 K
S	4 (2)	3 (1)
Na	6 (5)	1 (3)
C	27 (8)	24 (4)
N	26 (9)	16 (4)

Table 5. *Bond angles* (°)

| | X-ray 150 K | | X-ray 81 K | | |
	Conventional	High order	Conventional	High order	Neutron 94 K
S—C—N	179·09 (9)	179·20 (8)	179·14 (5)	179·10 (4)	179·09 (4)
C—S—Na	107·20 (2)	107·24 (2)	107·14 (2)	107·12 (2)	107·18 (4)
C—S—Na'	105·19 (3)	105·12 (3)	105·18 (3)	105·20 (3)	105·17 (4)
C—N—Na	144·19 (6)	144·18 (8)	144·67 (5)	144·64 (4)	144·47 (3)
C—N—Na'	110·81 (3)	110·73 (4)	110·67 (3)	110·65 (2)	110·77 (2)

These shifts are small compared with shifts of 0·008 and 0·009 Å in NaCN.2H₂O (Bats, 1977) for which fewer high-order reflections were measured.

Because of the temperature dependence of the positional parameters, it is not possible to compare directly X-ray and neutron atomic positions to assess any remaining asphericity shifts in the high-order positional parameters. It should be noted, however, that the librationally corrected CN bond length determined from the high-order X-ray refinements is 0·002 Å longer than the corresponding bond length determined with neutron diffraction. This difference may be due to a small shift of the N atom into its lone-pair direction in the high-order X-ray refinements resulting from a contribution of the N lone-pair scattering to the high-order X-ray intensities. A similar effect has been found in NH₄SCN (following paper).

Electron density analysis

In order to investigate the chemical bonding in NaSCN, deformation density maps have been calculated in a number of sections through the structure with both the 150 and 81 K data.

The calculations are based on the atomic parameters and scale factors from the high-order X-ray refinements. The standard deviations in the electron density (average value over the unit cell), based on the errors in

the observed structure factors, are 0·031 and 0·028 e Å⁻³ respectively, for the 150 and 81 K structure. Larger errors occur, however, at the symmetry sites and near the atomic nuclei.

Fig. 2 shows sections through the structure in the mirror plane. The 150 and 81 K maps are very similar, except close to the Na and S nuclei where the denisty may be strongly affected by uncertainties in the scale factors of the order of about 1%.

As the thermal motion is almost a factor two smaller at 81 K, the 81 K map should show the deformation density in greater detail. The CN overlap population and the N lone-pair peak are indeed slightly higher, by amounts 0·05 and 0·11 e Å⁻³ respectively, but the peak heights in the CS bond and S lone pairs are identical. The latter features are rather diffuse even at 81 K and therefore not very dependent on additional thermal smearing. The overall increase in detail of the deformation density on reduction of the temperature is fairly minor.

Difference density maps based on the atomic parameters and scale factors from the conventional X-ray refinements are shown in Fig. 3 for comparison purposes. These maps are similar to those in Fig. 2, as the difference between the conventional and high-order X-ray parameters is small. In general, difference maps from conventional X-ray refinements badly underestimate the deformation density; for example, such a
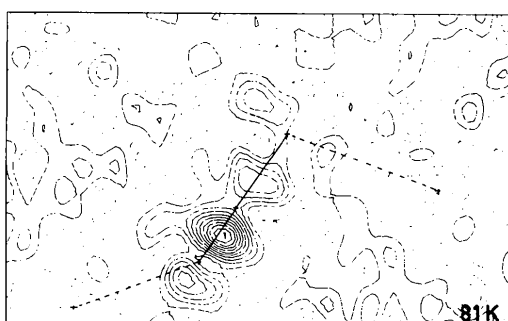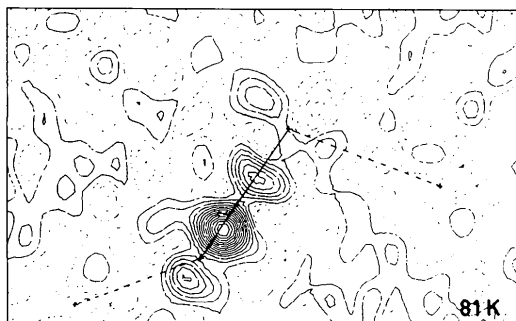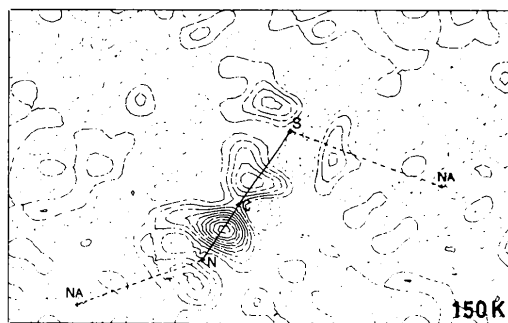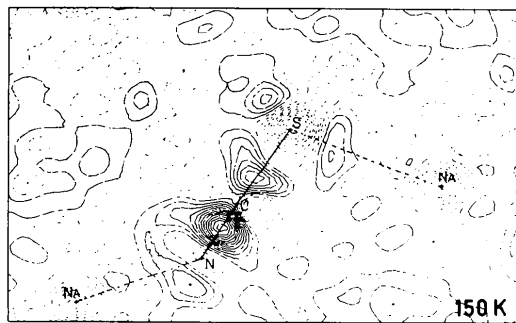

Fig. 2. Deformation density in section in the mirror plane, based on parameters from high-order X-ray refinements. Fourier synthesis with sin $\theta/\lambda \leq 0.75$ Å⁻¹. Contour interval 0·05 e Å⁻³; negative contours broken.

Fig. 3. Deformation density in section in the mirror plane, based on parameters from conventional X-ray refinements. Data cut-off and contour intervals as in Fig. 2.

difference map of NaCN.2H$_2$O was found to be almost featureless (Bats, 1977). The similarity of the maps in the present study is attributed to the high resolution made possible by the lower thermal motion of NaSCN.

Fig. 4 shows deformation density sections normal to the SCN axis through the CN and CS bond peaks. The density in the bond areas is almost cylindrically symmetric, as could be expected for a linear molecule.

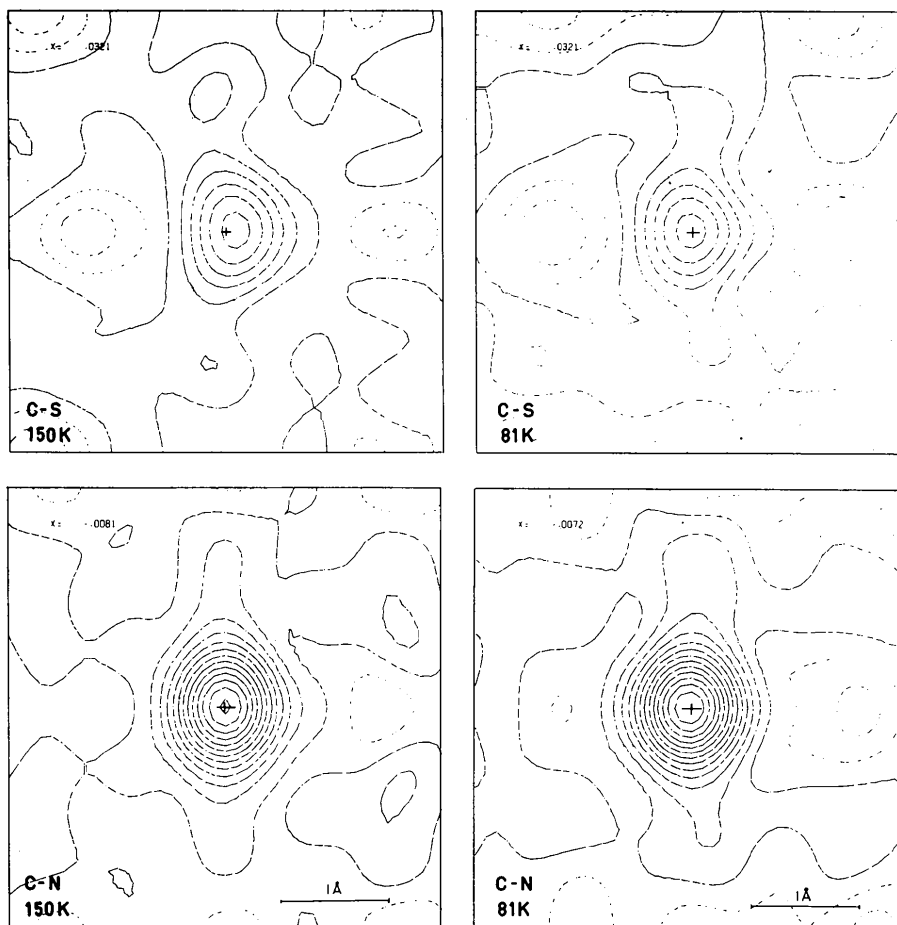The deformation density around the C and N atoms

Fig. 4. Deformation density sections through the CN and CS bond peaks, normal to the bonds. Contours as in Fig. 2.
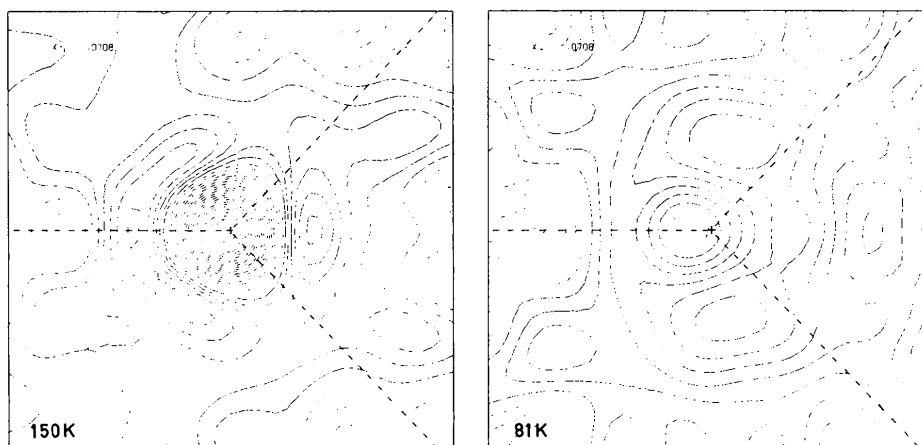

Fig. 5. Deformation density in a section normal to the CS bond, through the S lone-pair density. Fourier synthesis with sin $\theta/\lambda \leq 0.65$ Å^{-1}. Contour interval 0·25 e Å^{-3}; negative contours broken. Directions of Na atoms surrounding S are indicated.

(Fig. 2) agrees with the density expected for *sp*-hybridized atoms. Of interest is the position of the S lone-pair density which provides information about the hybridization, state of this atom. In contrast to the *sp*-hybridized N atom, there is no lone-pair density but an electron-deficient region at the back of the S atom (Fig. 2), while lone-pair peaks of about 0.15 e Å^{-3} are found at its sides. Cross-sections perpendicular to the CS axis through the S lone-pair density are shown in Fig. 5. It is not clear whether the lone-pair electrons form a continuous ring of density around the S atom or are localized in a number of discrete peaks as a result of intermolecular interactions. The peak heights of these lone pairs (0.15 e Å^{-3}) are too low compared with the experimental accuracy to show this feature in great detail.

As the S lone-pair density is found at angles of about 95–100° with the CS bond axis, the S atom appears almost unhybridized with the lone-pair electrons concentrated in the $3s$ and $3p\pi$ atomic orbitals. This is in agreement with results obtained from cyclooctasulfur (Coppens, Yang, Blessing, Cooper & Larsen, 1977). Partial back-donation of some π lone-pair density from the S atom towards the CN group would allow for the formation of the partial double CS bond, found in the present study.

The valence density, *i.e.* the observed total density minus the core density of the free atoms, has been calculated from the 150 K X-ray data. A section in the mirror plane is shown in Fig. 6. The map is dominated by the valence shells of the S, C and N atoms and bonding features are less apparent.

The theoretical deformation density for the SCN⁻ ion has been calculated for comparison with the experimental results, with the extended *ab initio* molecular wavefunctions for SCN⁻ of McLean & Yoshimine (1967) and subtracting free atoms, calculated from Clementi's (1965) atomic orbitals. A section through the SCN axis is shown in Fig. 7. It should be mentioned that the geometry of the SCN⁻ group taken by McLean & Yoshimine (CN bond 1.217, CS bond 1.561 Å) differs somewhat from the experimental geometry. But, for a qualitative comparison with experiment, this should not be a major consideration.

There is indeed a good resemblance between the theoretical and experimental deformation density. The CS, CN bond peaks and the nitrogen lone-pair peaks are almost similar in shape in the experimental and theoretical maps, but higher in the theoretical map in which thermal smearing has not been taken into account. The diffuse ring of lone-pair density around the S atom with a peak height of 0.15 e Å^{-3} is reproduced in the theoretical map, which also shows detail near the S nucleus. Such detail is not experimentally accessible because of thermal smearing, data cut-off and experimental errors which peak near the nucleus.

A quantitative comparison of the experimental and dynamical theoretical density in thiocyanates and related compounds is presently in progress (Bats & Feil, 1977).

Charge transfer

The bonding between Na and SCN would, from a classical point of view, be expected to be ionic. But, it is known that net charges in a crystal are in general considerably smaller than predicted by a pure ionic model (Slater, 1965; Pauling, 1948).

In order to determine the charge transfer from the Na atom towards the SCN group, the numerical integration method developed by Coppens (1975) has been applied to the 150 K data set. Integration was performed over the deformation density, as the diffuse nature of the Na valence shell makes integration over the valence density less meaningful.

Boundaries between the Na and SCN groups are defined by points with the same ratio of effective radii to neighboring atoms, as described by Coppens (1975). Effective radii assigned to the S, C and N atoms are 1.85, 1.5 and 1.5 Å.
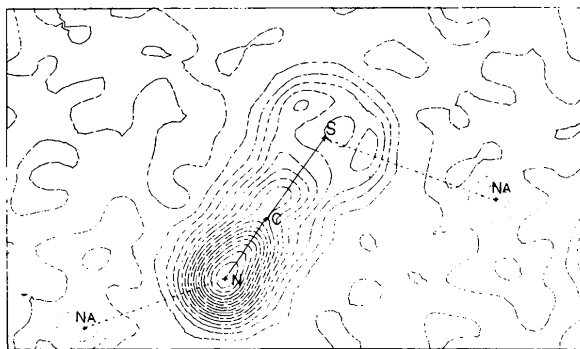

Fig. 6. Observed valence density in section in the mirror plane. Fourier synthesis with $\sin\theta/\lambda \leq 0.75$ Å^{-1}. Contour interval 0.2 e Å^{-3}; negative contours broken.
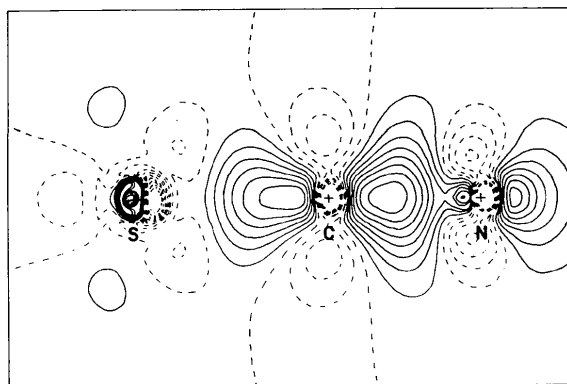

Fig. 7. Theoretical deformation density for SCN⁻. Contour interval 0.1 e Å^{-3}; negative and zero contours broken.

Table 7. *Net charge* (e) *on the sodium atom determined by numerical integration*

Effective radius (Å)	NaCN.2H$_2$O^a		Na sulfanilate.2H$_2$O^b		NaSCN (150 K)	
	Net charge	V^* (Å^3)	Net charge	V (Å^3)	Net charge	V (Å^3)
0·90	+0·15 (7)	5·3	+0·10 (7)	5·3	+0·20 (8)	4·8
1·05	+0·16 (6)	7·2	+0·11 (7)	7·4	+0·22 (7)	7·0
1·20	+0·14 (6)	9·9	+0·11 (7)	10·3	+0·24 (7)	9·4
1·35	+0·10 (5)	12·9	+0·08 (6)	13·7	+0·26 (6)	12·4
1·50	+0·05 (4)	16·7	+0·07 (6)	17·8	+0·27 (6)	15·8
1·65	0·00 (3)	21·0	+0·05 (6)	22·6	+0·28 (6)	20·0
1·80	−0·06 (3)	26·1	+0·05 (7)	27·5	+0·25 (6)	23·9
1·95	−	−	−	−	+0·24 (8)	28·8

References: (a) Bats (1977). (b) Bats & Coppens (1977).
* Volume of integration.

Table 8. *Net charges* (e) *in* NaSCN *and* NH$_4$SCN *determined by numerical integration and by least-squares refinement*

		Net charge (integration)	Volume* (Å^3)	Net charge (least squares)
NaSCN	SCN	−0·27 (6)	59·5	−0·20 (3)
	Na	+0·27 (6)	15·8	+0·20 (3)
NH$_4$SCN	SCN	−0·53 (4)	66·0	−0·74 (8)
	NH$_4$	+0·53 (4)	29·0	+0·74 (8)

* Volume of integration.

A problem arises as the Na atom is generally considered to be involved mainly in ionic or metallic bonding; consequently no comparable van der Waals radius is defined. A value for an effective Na radius was therefore introduced as a variable. The net charges on the Na atoms, resulting from the charge integration, are reported in Table 7 for a variety of radii and compared with results on NaCN.2H$_2$O and Na sulfanilate.2H$_2$O (Bats, 1977; Bats & Coppens, 1977).

Standard deviations assigned to the net charges observed are derived from the errors in the observed structure factors following an approximate method as described by Coppens & Hamilton (1968), and from relative errors in the scale factor of 1%. We note that the charges reported in Table 7 are fairly independent of the effective radius assigned to the Na atom. An effective radius of 1·5 Å will therefore be used here.

Net charges for both NaSCN and NH$_4$SCN obtained with the integration method, are reported in Table 8 and are compared with results of the occupancy refinement of a valence shell with adjustable orbital exponent (Coppens, Pautler & Griffin, 1971; Yang, Becker & Coppens, 1977).

The agreement between the results of the integration method and the least-squares projection method is reasonable. Negative charges considerably smaller than a completely ionic model would predict are found for both thiocyanate anions.

The net charge of +0·27 (6) e found on the Na atom

shows that the bonding in NaSCN is only partly ionic. The positive charge on Na is in between values of about +0·4 and +0·5 e reported for kernite (Cooper, Larsen, Coppens & Giese, 1973) and +0·1 e found for NaCN.2H$_2$O and Na sulfanilate.2H$_2$O (Bats, 1977; Bats & Coppens, 1977) (Table 7).

References

BATS, J. W. (1977). *Acta Cryst.* **B33**, 466–472.
BATS, J. W. & COPPENS, P. (1977). To be published.
BATS, J. W. & FEIL, D. (1977). To be published.
BECKER, P. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147.
BECKER, P. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
BLESSING, R. H., COPPENS, P. & BECKER, P. (1974). *J. Appl. Cryst.* **7**, 488–492.
CHIPMAN, D. R. (1969). *Acta Cryst.* **A25**, 209–213.
CLEMENTI, E. (1965). *Tables of Atomic Functions*, suppl. to *IBM J. Res. Dev.* **9**, 2–19.
COOPER, W. F., LARSEN, F. K., COPPENS, P. & GIESE, R. F. (1973). *Amer. Min.* **58**, 21–31.
COPPENS, P. (1975). *Phys. Rev. Lett.* **35**, 98–100.
COPPENS, P. & HAMILTON, W. C. (1968). *Acta Cryst.* **B24**, 925–929.
COPPENS, P., PAUTLER, D. & GRIFFIN, J. F. (1971). *J. Amer. Chem. Soc.* **93**, 1051–1058.
COPPENS, P., ROSS, F. K., BLESSING, R. H., COOPER, W. F., LARSEN, F. K., LEIPOLDT, J. G., REES, B. & LEONARD, R. (1974). *J. Appl. Cryst.* **7**, 315–319.
COPPENS, P., YANG, Y. W., BLESSING, R. H., COOPER, W. C. & LARSEN, F. K. (1977). *J. Amer. Chem. Soc.* In the press.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

STRUCTURE DETERMINATION OF NaSCN AT REDUCED TEMPERATURES

KVICK, Å., KOETZLE, T. F., THOMAS, R. & TAKUSAGAWA, F. (1974). *J. Chem. Phys.* **60**, 3866–3874.
MCLEAN, A. D. & YOSHIMINE, M. (1967). *Tables of Linear Molecule Wave Functions*, suppl. to *IBM J. Res. Dev.* **12**, 206–233.
MOKUOLU, J. A. A. & SPEAKMAN, J. C. (1975). *Acta Cryst.* **B31**, 172–176.
PAULING, L. (1948). *J. Chem. Soc.* pp. 1461–1467.
SHULL, C. G. (1971). *Coherent Neutron Scattering Amplitudes*, Table MIT.

SLATER, J. C. (1965). *Quantum Theory of Molecules and Solids*, Vol. 2. p. 108. New York: McGraw-Hill.
THORNLEY, F. R. & NELMES, R. J. (1974). *Acta Cryst.* **A30**, 748–757.
VAN ROOYEN, P. H. & BOEYENS, J. C. A. (1975). *Acta Cryst.* **B31**, 2933.
YANG, Y. W., BECKER, P. & COPPENS, P. (1977). To be published.

Acta Cryst. (1977). **B33**, 1542–1548

The Experimental Charge Distribution in Sulfur-Containing Molecules. A Study of the Deformation Density in NH₄SCN at 81 K by Combined X-ray and Neutron Diffraction*

BY J. W. BATS† AND P. COPPENS

*Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214, USA
and Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York 11973, USA*

(*Received 2 August* 1976; *accepted* 20 *October* 1976)

The crystal structure of NH₄SCN has been redetermined at 81 K by an accurate X-ray and neutron diffraction study. The CS and CN bond lengths are 1·649 (1) and 1·176 (1) Å. The intermolecular bonding consists of two N–H···N and two N–H···S hydrogen bonds of intermediate strength. The deformation density in the SCN group is very similar to results obtained for NaSCN. Deformation density maps through the hydrogen bonds support the electrostatic nature of the hydrogen bond. The charge transfer from the NH₄ group towards the SCN group has been determined as 0·5–0·6 e.

Introduction

A determination of the electron density distribution in NaSCN by X-ray diffraction is described in the preceding paper (Bats, Coppens & Kvick, 1977). As possible differences between the electron density distribution in related structures are of interest, a similar study of NH₄SCN was undertaken.

Since the ammonium group contains four H atoms whose parameters cannot be obtained from the X-ray experiment, accurate neutron data are essential for the present study. A temperature of 81 K was selected for the combined X-ray and neutron experiment. This temperature can be reached in both experiments.

The room-temperature structure of NH₄SCN has previously been refined by Zavodnik, Zvonkova, Zhdanov & Mirevick (1972). No parameters for the H

atoms were reported in that work, so that a further point of interest in the present study is the elucidation of the hydrogen-bond system in the NH₄SCN crystals.

Experimental

Neutron diffraction

Neutron diffraction data were collected at the high-flux beam reactor at Brookhaven National Laboratory. A parallelepiped-shaped crystal, 2·1 × 1·6 × 0·8 mm, was obtained from a methanol solution and mounted in a liquid-nitrogen-cooled cryostat. A thermocouple inside the cryostat recorded a temperature of 81·4 ± 0·1 K during the entire experiment. A calibration of the thermocouple using the ferromagnetic phase transition of an FeF₂ single crystal, mounted in the same way as the NH₄SCN specimen, indicated that the actual crystal temperature is within 0·8° of the recorded temperature.

* Work performed in part under the auspices of the US Energy Research and Development Administration.
† Present address: Chemical Physics Laboratory, Twente University of Technology, PO Box 217, Enschede, The Netherlands.