

The Experimental Charge Density in Sulfur-Containing Molecules: A Study of the Deformation Electron Density in Sulfamic Acid at 78 K by X-ray and Neutron Diffraction*

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(Received 19 April 1976; accepted 15 June 1976)

The deformation electron density in sulfamic acid (H_3NSO_3) has been determined by a combined X-ray and neutron diffraction study at 78 K. X–N maps show strong bond populations in all bonds. The nature of the S–N and S–O bonds is found to be similar to bonds between first-row atoms. The O atoms show single, fairly broad lone-pair peaks and are shifted towards the lone pairs in comparison with the neutron parameters. This shift disappears when only X-ray reflections with $\sin \theta/\lambda > 0.85 \text{ \AA}^{-1}$ are considered. A population analysis shows a net charge of +0.7 to +1.0 e on the S atom, –0.3 to –0.5 e on the O atoms and +0.12 e on the H atoms, while the N atom is close to neutral.

Introduction

Recent combined X-ray and neutron diffraction studies on single crystals have shown that it is possible to observe the bonding electrons in molecular crystals with sufficient precision to analyze the nature of the bonding. A recent review of this field is given by Coppens (1975).

In the framework of the study of the bonding in sulfur-containing compounds, the X–N technique has now been applied to sulfamic acid ($\text{H}_3\text{N–SO}_3$) at liquid nitrogen temperature. This compound has a relatively simple crystal structure (Sass, 1960), so that atomic parameters can be obtained with the high precision required for electron-density determination in spite of the small neutron scattering length of the sulfur atom. Of special interest is the nature of the O atoms, whose hybridization state is not easily predictable.

several times in liquid nitrogen in order to reduce extinction. Data were collected at the High Flux Beam Reactor at Brookhaven National Laboratory, on a computer-controlled diffractometer operating under the Multiple Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & Van Norton, 1966). The neutron wavelength was 1.0008 \AA , and the crystal was mounted in a liquid-nitrogen-cooled cryostat. Crystallographic information is given in Table 1. Data were collected in two octants up to a $\sin \theta/\lambda$ value of 0.80 \AA^{-1} , with a θ – 2θ step-scanning mode.

A thermocouple mounted inside the cryostat recorded a temperature during data collection varying from 78.8 to 79.4 K.

Two reflections were measured after every 50 reflections and the data were rescaled with respect to these standards. Except for a gradual increase in intensity

Experimental section and data reduction

Neutron diffraction

A crystal, grown from an aqueous solution, having a volume of 2.8 mm^3 and 15 developed boundary planes was selected for neutron diffraction. It was dipped

Table 1. *General information*

	Neutron	X-ray
<i>a</i>	8.036 (3) Å	8.034 (1) Å
<i>b</i>	8.025 (3)	8.020 (1)
<i>c</i>	9.236 (5)	9.236 (2)
<i>V</i>	595.6 (5) Å ³	595.1 (2) Å ³
Space group	<i>Pbca</i>	<i>Pbca</i>
Calculated density	2.165 g cm ^{–3}	2.167 g cm ^{–3}
Wavelength	1.0008 Å	0.71069 Å
($\sin \theta/\lambda$) _{max}	0.80 Å ^{–1}	1.23 Å ^{–1}
Total number of reflections	2995	7986
Unique reflections	1283	4484
Absorption coefficient	1.62 cm ^{–1}	8.548 cm ^{–1}
Transmission range	0.754–0.841	0.769–0.831

* Work performed in part under the auspices of the US Energy Research and Development Administration.

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totaling about 8% and resulting from an increase in incident-beam intensity during the reactor run (no incident-beam monitor was used), no significant fluctuations of the standards were observed. Because of the low energy of thermal neutrons radiation damage is not a likely contributor to this intensity increase.

The reflections have been corrected for the Lorentz effect and for absorption, with a linear absorption coefficient $\mu = 1.62 \text{ cm}^{-1}$ (which corresponds to an incoherent absorption cross-section for H of 40 barns) and a numerical integration over 144 grid points. A weighted average was calculated over symmetry-related reflections ($\Sigma |F^2 - \langle F^2 \rangle| / \Sigma F^2 = 3.6\%$). The weight of an averaged reflection was taken as the sum of the weights of the individual reflections. The weighting scheme adopted for the structure refinement was $w(F) = 4F^2[\sigma(F^2) + 0.03F^2]^{-2}$.

X-ray diffraction

A crystal grown from an aqueous solution, with dimensions $0.40 \times 0.35 \times 0.20 \text{ mm}$ and 14 developed boundary planes, was selected for the data collection. It was mounted in the cryostat described by Coppens, Ross, Blessing, Cooper, Larsen, Leipoldt, Rees & Leonard (1974) and kept at a temperature of 77.5 K . The cell constants given in Table 1 agree very well with those from the neutron diffraction experiment. Data were collected in a step-scanning mode (Blessing, Coppens & Becker, 1974) on a Picker diffractometer with Nb-filtered $\text{Mo K}\alpha$ radiation. The diffractometer was controlled by the Vanderbilt programming system (Lenhert, 1975). Two octants were measured up to $\sin \theta/\lambda$ values of 1.23 and 1.15 \AA^{-1} respectively.

Three standard reflections were measured after every 40 reflections and all data were rescaled with respect to these standards. The maximum fluctuation of the standards was about 2%.

The observed intensities were corrected for absorption by numerical integration over 64 grid points ($\mu = 8.548 \text{ cm}^{-1}$). Symmetry-related reflections were averaged after corrections for Lorentz and polarization effects and detector dead time (Chipman, 1969) ($\Sigma |F^2 - \langle F^2 \rangle| / \Sigma F^2 = 1.2\%$). The weight of an individual reflection was calculated from $w(I - B) = 1/\sigma^2(I - B)$ with $\sigma^2(I - B) = (I + B) + [0.03(I - B)]^2$ where I is the integrated intensity and B the background. The weight of the average used in the least-squares refinement was the sum of the weights of the individual reflections.

Structure refinement

Neutron diffraction

Initial positional parameters for sulfamic acid were taken from the room-temperature neutron diffraction

study of Sass (1960). Scattering lengths used for S, O, H and N are as follows: 0.2847 , 0.575 and -0.3723 (Shull, 1971) and $0.920 \times 10^{-12} \text{ cm}$ (Kvick, Koetzle, Thomas & Takusagawa, 1974).

Least-squares refinement of the positional and anisotropic thermal parameters showed that extinction was severe and anisotropic; it was treated as described by Becker & Coppens (1975). In order to save computing time, initial cycles of refinement were made on the data set in which the symmetry-related reflections were averaged. It was found that the extinction was best described by a type I crystal (mosaic-spread dominated), a Lorentzian distribution of the mosaic spread and anisotropy as described by Nemes & Thornley (1974), in agreement with the results obtained by Becker & Coppens (1975) for a variety of structures.

In order to allow fully for anisotropic extinction, the refinement was repeated on a data set in which symmetry-related reflections were not averaged. The positional parameters were identical with those from

Table 2. Fractional atomic coordinates

N Neutron, X1 X-ray $0.00 < \sin \theta/\lambda < 0.65$, X2 X-ray $0.00 < \sin \theta/\lambda < 1.23$, X3 X-ray $0.85 < \sin \theta/\lambda < 1.23$, X4 X-ray $1.00 < \sin \theta/\lambda < 1.23 \text{ \AA}^{-1}$.

Atom		x	y	z
S	N	0.16686 (11)	0.09279 (11)	0.17057 (10)
	X1	0.16682 (4)	0.09275 (4)	0.17060 (3)
	X2	0.16681 (1)	0.09278 (1)	0.17057 (1)
	X3	0.16680 (1)	0.09280 (1)	0.17056 (1)
	X4	0.16680 (2)	0.09281 (2)	0.17055 (2)
O(1)	N	0.05800 (6)	-0.05006 (6)	0.17826 (6)
	X1	0.5788 (12)	-0.05011 (13)	0.17839 (10)
	X2	0.05786 (4)	-0.05014 (3)	0.17834 (3)
	X3	0.05792 (4)	-0.05007 (4)	0.17830 (3)
	X4	0.05792 (6)	-0.05005 (5)	0.17828 (6)
O(2)	N	0.30657 (6)	0.07375 (6)	0.07391 (6)
	X1	0.30663 (11)	0.07375 (11)	0.07353 (11)
	X2	0.30659 (3)	0.07375 (4)	0.07368 (3)
	X3	0.30655 (4)	0.07376 (4)	0.07378 (3)
	X4	0.30653 (6)	0.07377 (6)	0.07378 (6)
O(3)	N	0.20178 (6)	0.17469 (6)	0.30570 (6)
	X1	0.20181 (12)	0.17483 (13)	0.30581 (10)
	X2	0.20177 (4)	0.17474 (4)	0.30578 (3)
	X3	0.20172 (4)	0.17471 (4)	0.30569 (3)
	X4	0.20173 (6)	0.17472 (7)	0.30565 (5)
N	N	0.03986 (4)	0.23958 (4)	0.07911 (3)
	X1	0.04007 (14)	0.023957 (13)	0.07905 (12)
	X2	0.03991 (4)	0.23953 (4)	0.07912 (3)
	X3	0.03987 (4)	0.23951 (4)	0.07919 (3)
	X4	0.03988 (5)	0.23958 (6)	0.07914 (6)
H(1)	N	0.09687 (14)	0.35517 (13)	0.07256 (13)
	X1	0.0837 (25)	0.3390 (29)	0.0776 (21)
	X2	0.0844 (13)	0.3389 (14)	0.0772 (11)
H(2)	N	-0.07152 (13)	0.25227 (14)	0.13397 (14)
	X1	-0.0489 (24)	0.2475 (23)	0.1287 (30)
	X2	-0.0491 (11)	0.2474 (12)	0.1273 (15)
H(3)	N	0.01470 (15)	0.19720 (14)	-0.02434 (12)
	X1	0.0196 (23)	0.2027 (20)	-0.0050 (22)
	X2	0.0204 (12)	0.2030 (10)	-0.0055 (11)

the previous refinement but the thermal parameters showed shifts of up to 1σ . An additional cycle of refinement in which the reflections most affected by extinction were excluded did not change any atomic parameter significantly and indicated that extinction had been treated adequately. The principal components of the g -tensor corresponded to mosaic spreads of approximately 2.8, 0.6 and 2.4". The final agreement indices are $R(F) = 4.1\%$, $R_w(F) = 3.4\%$ and the goodness of fit is $S = 1.01$.

A simultaneous refinement of the N scattering length gave as a result $b_N = 0.920(2) \times 10^{-12}$ cm, thus confirming the value of Kwick *et al.* (1974) used throughout this study.

The final positional and thermal parameters of the atoms are listed in Tables 2 and 3 respectively.*

* A list of structure factors for the neutron and X-ray data has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32014 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

X-ray diffraction

Initial positional parameters for all atoms were taken from Sass (1960). Scattering factors for the non-hydrogen atoms were from *International Tables for X-ray Crystallography* (1974); those for the H atoms were from Stewart, Davidson & Simpson (1965). For the S atom, the anomalous dispersion factors of Cromer & Liberman (1970) were applied.

Low-order reflections for which the observed and calculated structure factors were significantly different were checked for contributions from multiple reflections with the program *MULREF* (Coppens, 1968), but for none were multiple-reflection conditions satisfied, so that the differences must be interpreted otherwise.

An isotropic extinction refinement (Becker & Coppens, 1974) gave a mosaic spread corresponding to 16".

As parameters from an X-ray refinement may be biased considerably by bonding effects, especially when low-order data are dominant, refinements were made with data in various ($\sin \theta/\lambda$) ranges. H atoms and extinction parameters were not varied in the high-order

Table 3. Thermal parameters ($\times 10^5$, $\times 10^3$ for X-ray H)

For definition of symbols, see Table 2.

Atom		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	N	493 (35)	387 (36)	439 (39)	26 (26)	12 (29)	-30 (30)
	X1	555 (27)	463 (26)	460 (27)	43 (10)	-4 (9)	22 (9)
	X2	514 (3)	451 (3)	448 (3)	15 (2)	15 (2)	7 (2)
	X3	515 (2)	456 (2)	456 (2)	12 (2)	16 (2)	6 (2)
	X4	516 (2)	458 (2)	459 (3)	10 (3)	19 (3)	5 (3)
O(1)	N	975 (21)	528 (20)	844 (23)	-212 (15)	39 (16)	61 (16)
	X1	1024 (50)	605 (49)	909 (50)	-209 (39)	0 (30)	115 (31)
	X2	979 (8)	582 (7)	903 (8)	-235 (6)	15 (6)	90 (6)
	X3	985 (7)	591 (6)	897 (7)	-225 (6)	16 (6)	90 (5)
	X4	994 (9)	595 (9)	909 (12)	-225 (8)	22 (9)	94 (8)
O(2)	N	739 (20)	841 (21)	818 (24)	179 (15)	279 (15)	47 (16)
	X1	763 (46)	842 (46)	893 (52)	230 (31)	237 (36)	38 (34)
	X2	717 (7)	894 (8)	828 (8)	180 (6)	269 (6)	39 (6)
	X3	721 (6)	900 (7)	828 (7)	172 (6)	266 (5)	41 (6)
	X4	733 (8)	903 (11)	835 (11)	172 (8)	260 (8)	38 (8)
O(3)	N	889 (20)	829 (21)	561 (22)	17 (15)	-125 (15)	-130 (16)
	X1	891 (46)	1008 (50)	624 (49)	98 (35)	-138 (34)	-151 (35)
	X2	868 (7)	941 (8)	555 (7)	36 (7)	-34 (6)	-156 (6)
	X3	870 (7)	932 (7)	563 (6)	26 (6)	-128 (5)	-147 (5)
	X4	873 (9)	938 (10)	569 (9)	38 (9)	-131 (8)	-144 (8)
N	N	669 (14)	531 (14)	628 (16)	66 (9)	-40 (10)	66 (10)
	X1	707 (54)	592 (55)	574 (59)	81 (37)	-57 (37)	13 (41)
	X2	682 (7)	622 (8)	627 (8)	78 (6)	-47 (6)	39 (6)
	X3	689 (6)	637 (7)	626 (7)	72 (6)	-46 (6)	36 (5)
	X4	692 (9)	643 (10)	634 (10)	66 (8)	-48 (8)	33 (8)
H(1)	N	2459 (48)	1315 (41)	3612 (63)	-377 (35)	-626 (43)	519 (39)
	X1	24 (5)					
	X2	27 (3)					
H(2)	N	1784 (43)	3086 (53)	2474 (54)	797 (38)	667 (39)	622 (43)
	X1	17 (5)					
	X2	19 (2)					
H(3)	N	3053 (51)	2542 (50)	1335 (47)	522 (41)	-625 (39)	-263 (39)
	X1	13 (4)					
	X2	17 (2)					

Table 4. *Review of X-ray refinements*

($\sin \theta/\lambda$) _{min}	Number of ($\sin \theta/\lambda$) _{max}	Number of reflections	Number of variables	$R(F)$	$R_w(F)$	S^\dagger	Scale
0.00	0.65	666	59	2.0%	3.1%	2.57	6.728 (26)
0.00	1.23	4265	59	2.8	2.6	1.43	6.710 (6)
0.65	1.23	3599	46	3.1	2.3	1.07	6.734 (8)
0.85	1.23	2776	45	4.0	2.6	1.05	6.734*
1.00	1.23	1859	45	5.1	3.2	1.08	6.734*
0.65	0.85	823	45	1.3	1.6	1.07	6.734*
0.85	1.00	916	45	2.3	1.8	0.97	6.734*

* Not varied.

$$\dagger S = [\sum w(F_o - F_c)^2 / (NO - NV)]^{1/2}.$$

refinements with $\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$. The scale factor was highly correlated with the thermal parameters in all high-order refinements and therefore was not varied, except for the full $\sin \theta/\lambda$ range $0.65\text{--}1.23 \text{ \AA}^{-1}$ which showed no correlation terms larger than 0.71.

Table 4 lists the X-ray refinements with their agreement indices and scale factors. The positional and thermal parameters resulting from the low-order, conventional (all data) and high-order refinements are included in Tables 2 and 3.

Discussion of the structure

Bond lengths and angles calculated from the X-ray and neutron parameters are listed in Tables 5 and 6. Neutron bond lengths vibrationally corrected according to the rigid-body analysis of Schomaker & Trueblood (1968) are included in Table 5. The thermal parameters of the H atoms were excluded from the rigid-body analysis, as they contain a large component due to internal NH bending vibrations. The vibrational corrections to the bond lengths are found to be about 0.003 \AA .

The observed bond lengths and angles agree within experimental errors with those of the room-temperature study by Sass (1960).

The hydrogen-bond geometries obtained with the neutron parameters are listed in Table 7. The structure includes three strong hydrogen bonds with $N \cdots O$ interatomic distances varying from 2.930 to 2.964 \AA . Two $N \cdots O$ interactions with lengths 2.914 and 2.922 \AA and $N\text{--}H \cdots O$ angles 110 and 113° respectively

are also included in Table 7. It is debatable whether these interactions should be described as hydrogen bonds.

Two additional contacts between N and O(2) with an $N \cdots O$ distance of 2.784 \AA but with $N\text{--}H\text{--}O$ angles

Table 5. *Bond lengths (Å)*

	X-ray (conventional)	Neutron	Neutron (corrected)
S—O(1)	1.4440 (3)	1.4430 (10)	1.446
S—O(2)	1.4440 (3)	1.4423 (10)	1.445
S—O(3)	1.4389 (3)	1.4380 (11)	1.441
S—N	1.7714 (3)	1.7721 (9)	1.775
N—H(1)	0.87 (1)	1.0358 (11)	—
N—H(2)	0.84 (1)	1.0333 (10)	—
N—H(3)	0.85 (1)	1.0341 (11)	—

Table 6. *Bond angles (°)*

	X-ray (conventional)	Neutron
O(1)—S—O(2)	114.72 (2)	114.71 (7)
O(1)—S—O(3)	115.98 (2)	116.00 (7)
O(2)—S—O(3)	115.73 (2)	115.70 (7)
N—S—O(1)	101.68 (2)	101.67 (6)
N—S—O(2)	102.86 (2)	102.92 (6)
N—S—O(3)	102.84 (2)	102.83 (5)
S—N—H(1)	112.4 (7)	111.60 (7)
S—N—H(2)	106.6 (8)	109.30 (7)
S—N—H(3)	108.4 (6)	109.53 (7)
H(1)—N—H(2)	107 (1)	108.86 (10)
H(1)—N—H(3)	112 (1)	109.07 (10)
H(2)—N—H(3)	111 (1)	108.42 (10)

Table 7. *Hydrogen bonds (neutron parameters)*

N—H \cdots O	N \cdots O (Å)	H \cdots O (Å)	\angle N—H—O (°)	Classification
N—H(1) \cdots O(2')	2.952 (1)	1.918 (1)	175.56 (11)	Strong
N—H(2) \cdots O(3')	2.964 (1)	2.004 (1)	153.24 (10)	Strong
N—H(3) \cdots O(1')	2.930 (1)	1.938 (1)	159.54 (10)	Strong
N—H(2) \cdots O(1'')	2.914 (1)	2.353 (1)	112.81 (9)	Weak
N—H(3) \cdots O(3'')	2.922 (1)	2.404 (2)	109.92 (10)	Weak

of 91 and 93° respectively are not considered to contribute significantly to the bonding.

The S—O(3) bond distance is approximately 0.005 Å shorter than S—O(1) and S—O(2). This result is consistent with the observation (Table 7) that the N—H(2)···O(3) hydrogen bond is somewhat weaker than the other two strong hydrogen bonds.

The present study shows that the bond angles around the N atom are considerably closer to the true tetrahedral angle of 109.45° than found by Sass (1960).

The S—N bond distance of 1.775 Å should correspond to a single S—N bond, as in the zwitterion configuration the N atom has no valence electrons available to form a π bond with the sulfur *d* orbitals.

Comparison of X-ray and neutron parameters

Positional parameters

Atomic parameters obtained from X-ray studies can be considerably biased by bonding effects. As these bonding effects are mainly limited to reflections in the low-order region, improved atomic parameters have been obtained by refinement on high-order reflections alone. The ideal lower cut-off of these high-order refinements should depend on the compactness of the valence shells of the atoms present. For compounds containing first-row atoms, this cut-off is usually taken as $\sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$; *i.e.* the limit of the Cu sphere. Recent studies, however, have indicated that even these high-order refinements may still be slightly biased by bonding effects; O atoms for example often show shifts of 0.002 to 0.003 Å towards the lone-pair region in these refinements, indicating a valence-shell contribution to the high-order reflections. Theoretical evidence for this effect has been given by Dawson (1964) and Coppens (1969) who calculated for a prepared O atom that the relative change in scattering because of bonding effects is largest in the region with $\sin \theta/\lambda = 0.4\text{--}0.8 \text{ \AA}^{-1}$, while even for higher $\sin \theta/\lambda$ values these effects may not be negligible.

The availability of parameters from neutron diffraction together with the unusually large number of high-order X-ray reflections makes the present study

suitable for an analysis of asphericity shifts in the X-ray atomic parameters for different ranges in $\sin \theta/\lambda$.

Differences in atomic positions between our neutron and X-ray results for the non-hydrogen atoms are given in Table 8. The last column of Table 8 shows the shifts averaged over the three O atoms.

For the S and N atom no significant differences between the X-ray and neutron positions are found. The O atoms show small, but significant, shifts into the lone-pair regions in the low-order and conventional (all data) X-ray refinements [average shifts of 0.0022 (6) and 0.0015 (4) Å respectively]. This shift does not disappear completely in the high-order refinement for the $\sin \theta/\lambda$ range 0.65–1.23 Å^{-1} [average shift 0.0013 (4) Å but decreases to 0.0008 (4) Å when the lower $\sin \theta/\lambda$ cut-off is increased to 0.85 Å^{-1}]. However, the O atoms show a maximum shift in the $\sin \theta/\lambda$ range 0.65–0.85 Å^{-1} – average displacement 0.0024 (4) Å – in agreement with the arguments of Dawson (1964) and Coppens (1969)]. No further improvement in the positional parameters is obtained if the lower cut-off is increased from $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$ to $\sin \theta/\lambda = 1.00 \text{ \AA}^{-1}$; the remaining difference can therefore be attributed to experimental errors. This suggests that an X-ray refinement on data with $\sin \theta/\lambda$ larger than 0.85 Å^{-1} can be expected to give O positional parameters free of bonding effects. However, a recent 30 K X-ray and neutron diffraction study of *p*-nitropyridine *N*-oxide (Wang, Blessing, Ross & Coppens, 1976; Coppens & Lehmann, 1976) indicates that at this low temperature lone-pair scattering may even contribute to deformation densities beyond this limit.

Thermal parameters

Comparison of the thermal parameters (Table 3) from low- and high-order X-ray refinements shows large differences up to 10% attributed to bonding effects in the low-order refinement.

As bonding effects are expected to be minimal for the data beyond $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$, thermal parameters from a refinement on these data should be in good agreement with the neutron thermal parameters. U_{11} and U_{33} values agree well, but U_{22} values are

Table 8. X-ray asphericity shifts (shift of X-ray atomic position with respect to neutron position) (in Å)

$\sin \theta/\lambda$ range	S	O(1)	O(2)	O(3)	N	\bar{O}^*
0.00–0.65	0.0005 (9)	0.0016 (11)	0.0036 (10)	0.0015 (11)	0.0018 (11)	0.0022 (6)
0.00–1.23	0.0004 (9)	0.0015 (6)	0.0022 (6)	0.0008 (6)	0.0005 (4)	0.0015 (4)
0.65–1.23	0.0004 (9)	0.0016 (6)	0.0016 (6)	0.0007 (6)	0.0006 (4)	0.0013 (4)
0.85–1.23	0.0005 (9)	0.0007 (6)	0.0013 (6)	0.0005 (6)	0.0009 (4)	0.0008 (4)
1.00–1.23	0.0006 (9)	0.0007 (7)	0.0013 (7)	0.0006 (7)	0.0002 (5)	0.0009 (4)
0.65–0.85	0.0004 (9)	0.0032 (6)	0.0024 (6)	0.0017 (6)	0.0007 (5)	0.0024 (4)
0.85–1.00	0.0005 (9)	0.0008 (6)	0.0012 (6)	0.0003 (6)	0.0013 (5)	0.0008 (4)

* Average over three O atoms.

systematically lower in the neutron refinement (Table 3). A systematic error in one of the data sets could produce such a discrepancy. As both data sets have been carefully corrected for absorption and extinction and no obvious relation exists between the discrepancies and crystal orientation during data collection, the origin of these differences is not well understood. Systematic discrepancies have also been found in some other combined X-ray and neutron diffraction studies such as α -glycylglycine (Griffin & Coppens, 1975; Kvik, Koetzle & Stevens, 1977), sodium azide (Stevens & Hope, 1977) and ammonium tetraoxalate (Stevens, 1973) in which some thermal parameters were always systematically lower in the neutron refinement than in the high-order X-ray refinement. The possibility that discrepancies are due to differences between the X-ray and neutron TDS corrections in certain directions needs further exploration.

The deformation density

Deformation density maps based on the X-ray reflections with atomic parameters taken from the neutron refinement (X-N maps) showed significant differences in features among chemically identical atoms and bonds, which are attributed to systematic errors in the neutron thermal parameters, and eliminated in modified X-N maps with atomic parameters as obtained after rescaling to the results of the high-order X-ray refinement. In this way scale factors of 1.14 and 1.02 were applied to the neutron U_{22} and U_{33} values respectively.

X-N deformation density maps in a number of sections through the molecule are shown in Fig. 1, together with similar sections based on atomic parameters from the conventional and high-order ($\sin \theta/\lambda > 1.0 \text{ \AA}^{-1}$) X-ray refinements. The X-ray reflections with $\sin \theta/$

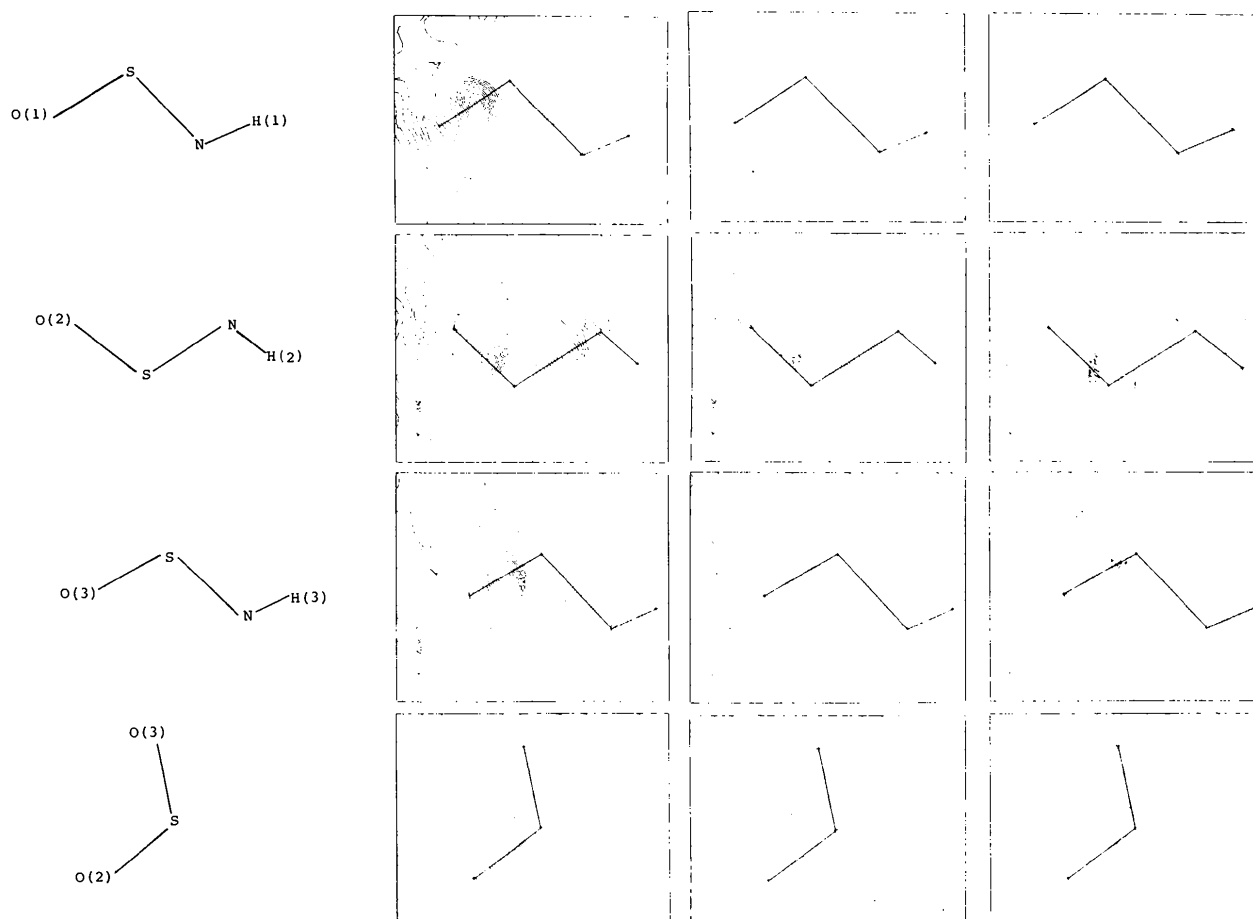


Fig. 1. Deformation density in sections through the molecule. Column 1: X-X (conventional), column 2: X-X (high order, $\sin \theta/\lambda > 1.0 \text{ \AA}^{-1}$), column 3: rescaled X-N maps. Data cut-off in Fourier synthesis: $(\sin \theta/\lambda)_{\max} = 0.85 \text{ \AA}^{-1}$. The contour interval is $0.05 e \text{ \AA}^{-3}$. Negative contours are shown as broken lines.

$\lambda < 0.85 \text{ \AA}^{-1}$ were used in calculating the maps; inclusion of higher-order reflections did not significantly affect the bonding features but rapidly increased the noise level of the maps. The high-order X-ray scale factor was applied to bring the observed structure factors onto an absolute scale.

There is a good agreement between the deformation maps based on the conventional and high-order X-ray parameters and the modified neutron parameters, except for features involving the H atoms, whose atomic parameters cannot be correctly obtained from the X-ray data.

The similarity of the X-X maps based on the conventional and high-order X-ray refinements suggests that the former refinement is largely dominated by the high-order reflections.

Strong peaks are found in all bonds in the molecule. Those in S-N and S-O bonds are similar to peaks in bonds between first-row atoms, with an accumulation of electron density in one maximum in the bond; this in contrast to the somewhat unusual appearance of the S-S bond in orthorhombic sulfur (Blessing, Cooper, Yang & Coppens, 1973).

Of interest is the nature of the O atoms, whose state of hybridization is less predictable than for most planar or linear compounds used so far in electron density studies. The bonding features around all three O atoms are cylindrically symmetric around the S-O bonds. The rather broad lone-pair peaks at the back of the O atoms should be compared with more compact O lone-pair peaks in inorganic carbonyl ligands in benzene-tricarbonylchromium (Rees & Coppens, 1973) and hexacarbonylchromium (Rees & Mitschler, 1975), where the C-O bond is essentially triple and the lone pair sp hybridized. On the other hand, organic CO groups in cyanuric acid (Coppens & Vos, 1971) and glycine (Almlöf, Kvik & Thomas, 1973) show double peaks or broad single maxima in the molecular plane, interpreted as approximate sp^2 hybrids. The present case seems to be intermediate between these two. The average extension of the lone-pair peak and its cylindrical symmetry would be compatible with the use of sp^n hybrids with $1 < n < 2$ and all three oxygen p orbitals contributing to the hybrid orbitals.

No significant lone-pair features have been found for the sulfate O atoms in taurine (O'Connell, 1969) or in a recent low-temperature study of Na-sulfanilate dihydrate (Bats, 1977). This is most likely due to an insufficient number of high-order X-ray reflections measured for those compounds.

The excess density at the nuclei on all three H atoms in the X-N maps is a result of the use in the difference maps of H atom scattering factors calculated from an isolated atom, while in bonded H atoms the electron density is known to be contracted with respect to free atoms.

The deformation density in cross-sections through

the S-N and S-O bonds given in Fig. 2 shows the cylindrical symmetry of the density in these bonds.

Cruickshank (1961) has interpreted the shortness of the SO bonds in sulfamic acid and other sulfate derivatives as evidence for $d_{\pi}-p_{\pi}$ contributions to the bond. A later extended Hückel MO study indicated that d orbitals are not absolutely essential as the bond length variation may also be explained in terms of s and p orbitals alone (Bartell, Su & Yow, 1970). Nevertheless, there is little doubt that the shortening with respect to the SO single bond ($l \sim 1.69 \text{ \AA}$) should correspond to double-bond character and an increased overlap population. An experimental analysis as done for single, double and triple CC and CN bonds (Helmholdt, Ruysink, Reynaers & Kemper, 1972; Becker, Coppens & Ross, 1973; Berkovitch-Yellin & Leiserowitz, 1975) may be performed when measurements on SO bonds of different length become available.

Deformation maps in sections through the hydrogen bonds are given in Fig. 3. The maps clearly show that there is no build up of density in the $H \cdots O$ bonds, in support of the electrostatic model of the hydrogen bond. The appearance of the deformation density in the hydrogen bonds shows a good resemblance to similar sections in α -glycylglycine (Griffin & Coppens, 1975; Kvik, Koetzle & Stevens, 1977) and 2-amino-5-chloropyridine (Kvik, Thomas & Koetzle, 1976).

Population analyses

It is possible to derive from the electron density net atomic populations valid within the definition of the

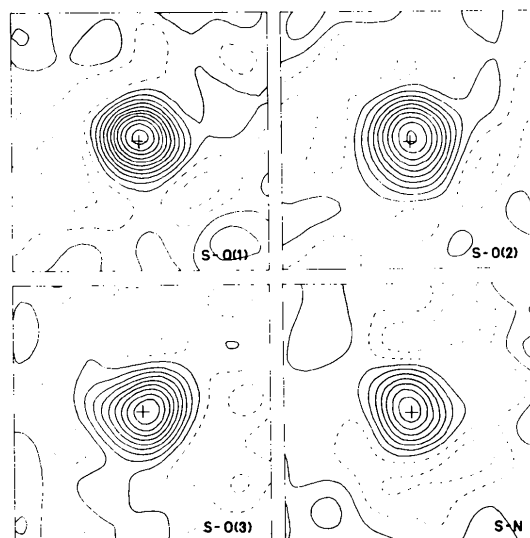


Fig. 2. Deformation density [$X-X$ (high order, $\sin \theta/\lambda > 1.0 \text{ \AA}^{-1}$)] in cross-sections through the S-O and S-N bonds. Data cut-off in Fourier synthesis: $(\sin \theta/\lambda)_{\max} = 0.75 \text{ \AA}^{-1}$. Contour intervals as in Fig. 1.

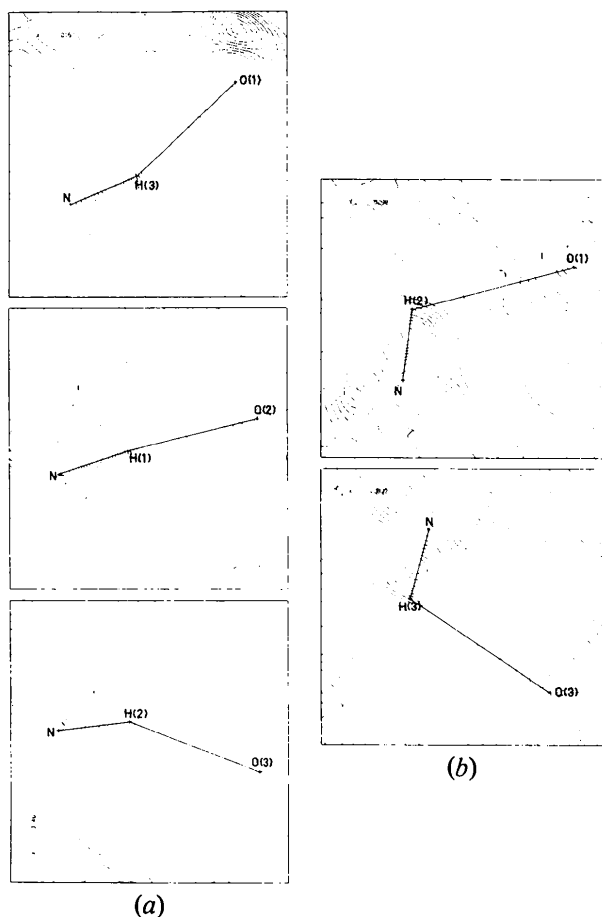


Fig. 3. Deformation density (rescaled X-N maps) in the planes of the hydrogen bonds. (a) Strong hydrogen bonds; (b) weak hydrogen bonds. Data cut-off in Fourier synthesis: $(\sin \theta/\lambda)_{\max} = 0.75 \text{ \AA}^{-1}$. Contour intervals as in Fig. 1.

atomic functions. This can be achieved by a projection of the observed density in a number of one-center functions. A simple approach is given by the valence-shell projection method (LS) of Stewart (1970) in which the population of the valence shell of each atom is considered as a variable, while the core populations and all other possible parameters are kept fixed. An extended version of this method is the extended valence-shell projection method (ELS) of Coppens, Pautler & Griffin (1971), who varied the valence-shell populations of the atoms simultaneously with the positional and thermal parameters and the scale factor. As the results of the ELS method were found to depend on the basis functions used, a further improvement was made by the κ -refinement (*RADIEL*) of Yang, Becker & Coppens (1977), in which the orbital exponent of the valence shell is refined together with the ELS parameters.

LS, ELS and *RADIEL* refinements for sulfamic acid are summarized in Table 9. Both core and valence scattering factors of the non-hydrogen atoms were derived

Table 9. Net atomic charges (e)

	LS	ELS	<i>RADIEL</i>
S	+0.89 (6)	+0.74 (6)	+1.03 (7)
O(1)	-0.32 (3)	-0.26 (3)	-0.45 (4)
O(2)	-0.40 (3)	-0.44 (3)	-0.61 (3)
O(3)	-0.21 (3)	-0.32 (3)	-0.53 (4)
N	-0.34 (4)	-0.07 (6)	+0.18 (10)
H(1)	+0.09 (3)	-0.01 (5)	+0.06 (5)
H(2)	+0.21 (3)	+0.16 (5)	+0.13 (5)
H(3)	+0.07 (3)	+0.20 (5)	+0.19 (5)
O (averaged)	-0.31 (2)	-0.34 (2)	-0.53 (3)
H (averaged)	+0.12 (2)	+0.12 (3)	+0.13 (3)

from Hartree-Fock atomic wave functions (Fukamachi, 1971), while the hydrogen scattering factors were taken from Stewart, Davidson & Simpson (1965).

Net charges are somewhat dependent upon the method. In the radial-dependence refinement, for example, the O atoms expand by 3% [$\kappa = 0.971$ (3)] and the O atoms accordingly accommodate a slightly higher negative charge. The general results are, however, similar for all three projection methods. The S atom has a large positive charge of about +0.7 to +1.0 e, in agreement with the appearance of this atom in the deformation density maps. Negative charges of -0.3 to -0.5 e are found for the O atoms and slightly positive charges of about +0.12 e for the H atoms. Only the net charge on the N atom depends strongly on the method used. In this case, we prefer the results of the more flexible refinement including the radial parameter which more easily accommodates changes in electron density upon molecule formation.

The authors would like to thank Dr G. J. B. Williams for assistance with the neutron data collection and Dr R. H. Blessing for help with the X-ray data collection. Partial support of this research by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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