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An Electron Density Study of Sodium Sulfanilate Dihydrate at 78 K

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The crystal structure of sodium sulfanilate dihydrate has been redetermined from single-crystal X-ray data collected at 78 K. Separate least-squares refinements were performed on the low-order data, the high-order data and the entire data set. The nonplanarity of the amino group has been reconfirmed. Difference density maps, based on the atomic parameters from the high-order refinement, are interpreted in terms of bonding effects. An analysis of the charge distribution led to net charges of −0·37 (4), +0·07 (4) and +0·15 (4) e for the sulfanilate group, Na atom and hydrate molecules respectively.

Introduction

The room-temperature crystal structure of sodium sulfanilate dihydrate ($H_2NC_6H_4SO_3Na.2H_2O$) has recently been reported (Bats & Coppens, 1975). In the framework of a study of the electron density distribution and chemical bonding in sulfur-containing compounds the structure has now been redetermined from accurate X-ray data collected at liquid nitrogen temperature. This study is of interest in comparison with a recent electron density study of sulfamic acid (Bats, Coppens & Koetzle, 1977). Of interest also will be a determination of the charge distribution in the sodium sulfanilate dihydrate structure.

Experimental

A single crystal of sodium sulfanilate dihydrate, grown from an aqueous solution, with dimensions 0·6 × 0·4 × 0·35 mm was selected for the data collection and mounted in the cryostat described by Coppens *et al.* (1974). The crystal was cooled to 78 K. The cell dimensions and space group are given in Table 1. Data were collected in four octants of reciprocal space up to $\sin\theta/\lambda$ values of 1·00, 0·90, 0·75 and 0·75 $Å^{-1}$ respectively, with Nb-filtered Mo $K\alpha$ radiation on a Picker FACS-I diffractometer in a step scanning mode (Blessing, Coppens & Becker, 1974). Three standard reflections, remeasured after every 40 reflections, showed a maximum fluctuation of about 2%. The data were rescaled with respect to these standards.

Excluding these standards a total of 18 096 reflections were obtained of which 5960 were unique.

Data were corrected for absorption ($\mu = 3{\cdot}83\ \mathrm{cm}^{-1}$; transmission range: 0·845–0·851), while coincidence losses of the counter were corrected as described by Chipman (1969).

Symmetry-related reflections were weight-averaged. The weight $w(F^2)$ of an individual reflection was derived from the counting statistics; the weight $w(\overline{F^2})$ of an average reflection was taken as the sum of the weights of the individual reflections. A small term proportional to the intensity was further added to the standard deviations: $w(\overline{F^2}) = [\sigma(\overline{F^2}) + k\overline{F^2}]^{-2}$; a value $k = 0{\cdot}02$ was derived from the variation in symmetry-related reflections. 5662 average reflections had $I > 0$ and were used for the structure refinement.

Table 1. *Crystallographic information*

	78 K*	295 K †
a	23·924 (7) Å	23·895 (5) Å
b	10·006 (1)	10·101 (2)
c	7·932 (1)	7·944 (2)
V	1898·8 (6) $Å^3$	1917·4 (7) $Å^3$
Space group	*Pbca*	*Pbca*

* Present study.
† Bats & Coppens (1975).

Table 2. *Survey of least-squares refinements*

	Low order	Conventional	High order
$(\sin\theta/\lambda)_{\min}$ ($Å^{-1}$)	0·00	0·00	0·65
$(\sin\theta/\lambda)_{\max}$ ($Å^{-1}$)	0·65	1·00	1·00
Number of reflections	2139	5662	3521
Number of variables	167	167	127
Scale factor	2·412 (4)	2·398 (2)	2·379 (7)
$R(F)$ (%)	2·7	3·9	4·9
$Rw(F)$ (%)	3·7	3·8	3·6
Goodness of fit*	2·12	1·59	1·06

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

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Structure refinement

Initial positional parameters for all the atoms were taken from the room-temperature study by Bats & Coppens (1975). Scattering factors for the non-hydrogen atoms were as listed in *International Tables for X-ray Crystallography* (1974), while for the H atoms the molecular optimized scattering factors of Stewart, Davidson & Simpson (1965) were used. For the S and Na atoms, the anomalous scattering factors of Cromer & Liberman (1970) were applied.

In order to study the influence of bonding effects on the least-squares parameters, separate refinements were done on the low-order data, the high-order data and on all the data (conventional refinement). The atomic parameters of the H atoms were not varied in the high-order refinement. Extinction was found to be negligible.

A survey of the least-squares refinements is given in Table 2. The positional parameters of the atoms are given in Table 3.*

Table 3. *Positional parameters* ($\times 10^5$ *for heavy atoms;* $\times 10^4$ *for* H)

	x	*y*	*z*
S	40273 (1)*	3880 (3)	5069 (4)
	40274 (1)	3881 (2)	5069 (2)
	40276 (1)	3883 (2)	5071 (2)
Na	48087 (2)	33678 (5)	−9192 (7)
	48087 (1)	33679 (3)	−9192 (4)
	48091 (2)	33683 (4)	−9195 (5)
O(1)	39640 (4)	−9446 (9)	−2671 (12)
	39640 (2)	−9449 (5)	−2676 (7)
	39638 (3)	−9451 (6)	−2693 (8)
O(2)	42767 (4)	13519 (9)	−6559 (11)
	42765 (2)	13513 (6)	−6563 (7)
	42764 (3)	13497 (7)	−6567 (9)
O(3)	43132 (4)	2973 (9)	21323 (12)
	43133 (2)	2969 (6)	21328 (7)
	43131 (3)	2966 (7)	21342 (8)
C(1)	33350 (5)	9122 (13)	9096 (16)
	33357 (3)	9124 (7)	9094 (9)
	33365 (3)	9127 (8)	9101 (9)
C(2)	30090 (6)	1293 (13)	19958 (16)
	30099 (3)	1281 (7)	19963 (9)
	30102 (3)	1275 (8)	19949 (10)
C(3)	24429 (6)	3801 (13)	21571 (17)
	24423 (3)	3790 (7)	21592 (9)
	24420 (3)	3785 (8)	21601 (10)
C(4)	21917 (5)	14380 (13)	12708 (16)
	21913 (3)	14370 (7)	12717 (9)
	21901 (3)	14352 (8)	12747 (10)
C(5)	25255 (5)	22455 (12)	2466 (16)
	25250 (3)	22460 (7)	2470 (9)
	25246 (3)	22474 (8)	2476 (9)
C(6)	30944 (5)	19840 (13)	501 (16)
	30947 (3)	19841 (7)	496 (9)
	30947 (3)	19844 (8)	481 (10)
N	16148 (5)	16364 (12)	14055 (15)
	16142 (3)	16374 (7)	14063 (9)
	16136 (3)	16386 (8)	14072 (10)
O(4)	47265 (4)	−27441 (10)	−17665 (12)
	47261 (2)	−27442 (6)	−17664 (8)
	47249 (3)	−27446 (7)	−17671 (9)
O(5)	44201 (4)	49002 (10)	10366 (13)
	44200 (3)	49009 (6)	10374 (8)
	44194 (3)	49033 (7)	10396 (9)
H(1)	3190 (5)	−591 (12)	2627 (15)
H(2)	2224 (5)	−186 (11)	2888 (16)
H(3)	2366 (5)	2989 (12)	−326 (15)
H(4)	3314 (5)	2563 (12)	−676 (15)
H(5)	1512 (6)	2398 (14)	984 (18)
H(6)	1473 (5)	1442 (13)	2440 (16)
H(7)	4494 (6)	−2255 (16)	−1424 (20)
H(8)	4547 (7)	−3442 (16)	−1968 (19)
H(9)	4110 (8)	5205 (16)	824 (22)
H(10)	4393 (6)	4516 (15)	1984 (19)

* First row: low-order refinement. Second row: conventional refinement. Third row: high-order refinement.

Discussion of results

The numbering of the atoms and a comparison of the thermal ellipsoids at 78 K and 295 K is shown in Fig. 1.

Differences in atomic positions between the three refinements are given in Table 4. Comparison of the atomic positions obtained from the low-order, conventional and high-order refinements shows that those of the S and Na atoms are identical in all three refinements, which can be attributed to the relatively heavy cores of these atoms.

Differences between the refinements are the largest for the C atoms, which tend to be shifted into the benzene ring in the low-order and conventional refinements by amounts of 0·002–0·006 Å and 0·001–0·003 Å

Table 4. *Asphericity shifts in atomic positions* (Å)

	HO–LO*	HO–CR*
S	0·0007 (3)	0·0004 (2)
Na	0·0010 (5)	0·0006 (4)
O(1)	0·0018 (9)	0·0016 (6)
O(2)	0·0024 (9)	0·0017 (7)
O(3)	0·0017 (9)	0·0012 (7)
O(4)	0·0040 (10)	0·0025 (7)
O(5)	0·0042 (10)	0·0030 (7)
C(1)	0·0036 (13)	0·0021 (8)
C(2)	0·0034 (13)	0·0016 (8)
C(3)	0·0035 (13)	0·0017 (8)
C(4)	0·0057 (13)	0·0033 (8)
C(5)	0·0030 (12)	0·0015 (8)
C(6)	0·0018 (13)	0·0009 (8)
N	0·0038 (12)	0·0025 (8)

* LO: low-order refinement. CR: conventional refinement. HO: high-order refinement.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32379 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

respectively. This effect is due to the large bond populations in the partial double C—C bonds.

The N atom is shifted into the C(4)—N bond by amounts of 0·004 and 0·002 Å respectively in the low-order and conventional refinements; this shift is expected to be due to the bond population in the partial double C—N bond.

The positional parameters of the sulfate O atoms do not show significant differences between refinements; the O atoms of the hydrate molecules, however, show a significant shift towards the expected lone-pair region in the low-order and conventional refinements when compared with the high-order parameters. These asphericity shifts may still be underestimated as O lone-pair electrons are known to scatter beyond the $\sin\theta/\lambda$ limit of 0·65 $Å^{-1}$, taken as the lower cut-off in the high-order refinement (Bats, Coppens & Koetzle, 1977; Wang, Blessing, Ross & Coppens, 1976).

Comparison of the thermal parameters resulting from the different refinements indicates an overall overestimation of the thermal motion in the low-order and conventional refinements, where the thermal parameters tend to compensate for bonding effects, as generally found in electron density studies.

Bond distances are given in Table 5 and reconfirm the above-mentioned asphericity shifts of the atoms. Bond angles are given in Table 6.

All bond angles are in good agreement with those from the previous room-temperature study (Bats & Coppens, 1975); all bond lengths in the sulfanilate group are considerably shorter in the room-temperature study, indicating the effect of librational shortening.

The **TLS** analysis of Schomaker & Trueblood (1968) has been applied to the sulfanilate group for both the room-temperature and low-temperature structures. H atoms were not included in this rigid-body analysis. The R values, defined as $R = \{\Sigma(U_{\text{obs}} - U_{\text{calc}})^2/\Sigma\, U^2_{\text{obs}}\}^{1/2}$ (where the subscripts obs and calc refer to the diffraction experiment and the rigid-body model respectively and where the summation is over the $6n$ thermal

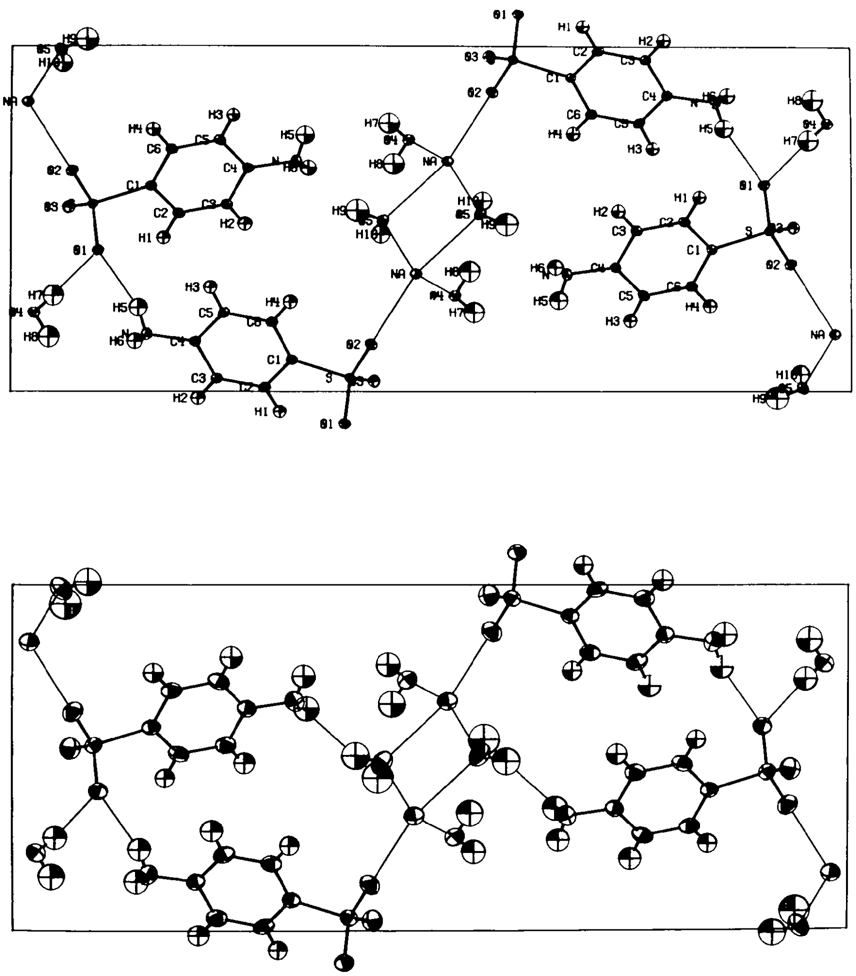

Fig. 1. The numbering of the atoms and a comparison of the thermal ellipsoids (50% probability) at 78 K (top) and 295 K (bottom).

parameters, n being the number of atoms in the rigid body), were 8·3 and 10·1% for the room-temperature and low-temperature data respectively. In the room-temperature case the relatively poor agreement between the observed thermal parameters and those calculated from the rigid-body parameters could be a result of the parameters being seriously affected by bonding; in the low-temperature case, however, high-order data were used, so the effect must be related to a significant non-rigid contribution to the sulfanilate motion.

A rigid-body analysis, treating the $N-C_6$ and $C(1)-SO_3$ groups separately, indeed showed significantly different motions for both groups and gave a considerably improved agreement between observed and calculated thermal parameters (the R value, defined above, now being 2·7% for the low-temperature thermal parameters). The change in bond-length corrections was minor, however.

Bond lengths corrected for librational shortening are given in Table 7 for the room-temperature and low-temperature studies. The agreement between the two sets has been improved by the corrections. Significant differences between the two studies remain for some C–C and C–N bond lengths and are most likely due to bonding effects in the room-temperature study.

The six hydrogen bonds are listed in Table 8. Their lengths are slightly shorter at low temperature than at room temperature. A small shortening on cooling is also found for some of the Na–O bonds. Intermolecular interactions obviously tend to shorten as the thermal motion decreases, leading to unit-cell contraction on cooling.

Table 5. *Uncorrected bond lengths* (Å)

	Low order	Conventional	High order
S–O(1)	1·476 (1)	1·4763 (6)	1·4774 (7)
S–O(2)	1·462 (1)	1·4612 (6)	1·4601 (7)
S–O(3)	1·462 (1)	1·4626 (6)	1·4631 (7)
S–C(1)	1·767 (1)	1·7651 (8)	1·7638 (9)
C(1)–C(2)	1·402 (2)	1·403 (1)	1·403 (1)
C(2)–C(3)	1·383 (2)	1·387 (1)	1·388 (1)
C(3)–C(4)	1·406 (2)	1·406 (1)	1·405 (1)
C(4)–C(5)	1·397 (2)	1·398 (1)	1·402 (1)
C(5)–C(6)	1·395 (2)	1·397 (1)	1·398 (1)
C(1)–C(6)	1·395 (2)	1·396 (1)	1·397 (1)
C(4)–N	1·399 (2)	1·399 (1)	1·398 (1)
C(2)–H(1)	0·97 (2)	0·98 (1)	
C(3)–H(2)	0·96 (2)	0·96 (1)	
C(5)–H(3)	0·94 (2)	0·95 (1)	
C(6)–H(4)	0·97 (2)	0·98 (1)	
N–H(5)	0·87 (2)	0·86 (1)	
N–H(6)	0·91 (2)	0·91 (1)	
O(4)–H(7)	0·78 (2)	0·79 (2)	
O(4)–H(8)	0·84 (2)	0·82 (2)	
O(5)–H(9)	0·81 (2)	0·82 (2)	
O(5)–H(10)	0·84 (2)	0·83 (2)	

Na–O bonds	High order
Na–O(2)	2·397 (1)
Na–O(3)′	2·376 (1)
Na–O(4)′	2·419 (1)
Na–O(4)″	2·485 (1)
Na–O(5)	2·376 (1)
Na–O(5)′	2·531 (1)

Table 7. *Bond lengths corrected for libration* (Å)

	78 K	295 K
S–O(1)	1·480 (1)	1·477 (1)
S–O(2)	1·463 (1)	1·462 (1)
S–O(3)	1·466 (1)	1·462 (1)
S–C(1)	1·766 (1)	1·763 (2)
C(1)–C(2)	1·405 (1)	1·398 (2)
C(1)–C(6)	1·399 (1)	1·392 (2)
C(2)–C(3)	1·389 (1)	1·374 (2)
C(3)–C(4)	1·407 (1)	1·403 (2)
C(4)–C(5)	1·404 (1)	1·396 (2)
C(5)–C(6)	1·399 (1)	1·380 (2)
C(4)–N	1·399 (1)	1·391 (2)

Table 8. *Hydrogen bonds*

$X\cdots\mathrm{H}-Y$	$X\cdots Y$ (Å)	$X\cdots\mathrm{H}$ (Å)	$X-\mathrm{H}-Y$ (°)
O(1)···H(7)–O(4)	2·823 (1)	2·04 (2)	172 (2)
O(1)···H(6)′–N′	3·056 (1)	2·15 (2)	173 (1)
O(1)···H(5)″–N″	3·086 (1)	2·24 (2)	164 (2)
O(2)···H(10)′–O(5)′	2·925 (1)	2·08 (2)	176 (1)
O(3)···H(8)′–O(4)′	2·872 (1)	2·07 (2)	163 (1)
N···H(9)″–O(5)″	3·034 (1)	2·30 (2)	151 (2)

Table 6. *Bond angles* (°)

O(1)–S–O(2)	111·94 (4)	C(2)–C(3)–C(4)	120·59 (7)	C(4)–C(5)–H(3)	120·2 (7)
O(1)–S–O(3)	111·06 (4)	C(3)–C(4)–C(5)	118·81 (7)	C(6)–C(5)–H(3)	118·8 (7)
O(2)–S–O(3)	114·12 (4)	C(3)–C(4)–N	119·67 (7)	C(5)–C(6)–H(4)	117·8 (7)
C(1)–S–O(1)	104·32 (4)	C(5)–C(4)–N	121·50 (7)	C(1)–C(6)–H(4)	122·6 (7)
C(1)–S–O(2)	107·50 (4)	C(4)–C(5)–C(6)	120·91 (7)	C(4)–N–H(5)	112·3 (9)
C(1)–S–O(3)	107·24 (4)	C(5)–C(6)–C(1)	119·54 (7)	C(4)–N–H(6)	114·1 (8)
S–C(1)–C(2)	117·80 (6)	C(1)–C(2)–H(1)	118·9 (7)	H(5)–N–H(6)	116 (1)
S–C(1)–C(6)	121·86 (6)	C(3)–C(2)–H(1)	121·1 (7)	H(7)–O(4)–H(8)	102 (1)
C(2)–C(1)–C(6)	119·98 (7)	C(2)–C(3)–H(2)	118·6 (7)	H(9)–O(5)–H(10)	107 (1)
C(1)–C(2)–C(3)	120·10 (7)	C(4)–C(3)–H(2)	120·8 (7)		

Analysis of the chemical bonding

Electron density analysis

A difference density map in the plane of the benzene ring, based on the atomic parameters from the high-order refinement, is shown in Fig. 2. The scale factor from the conventional refinement has been used in the calculation of this map. Based on its consistency in all three X-ray refinements (Table 2) an error of about 1% in this scale factor is expected. A difference density synthesis based on the atomic parameters from the conventional refinement was found to be very similar to Fig. 2, though the peak heights were slightly lower.

Peaks of well defined shapes with maximum heights of 0·45 to 0·57 eÅ^{-3} are found in every C—C and C—N bond in Fig. 2. The similarity of identical bonds supports the accuracy of this study. A single peak with a maximum height of 0·49 eÅ^{-3} is found in the C(1)—S bond.

Deformation density maps in cross-sections through the midpoints of the C—C, C—N and C—S bonds are shown in Fig. 3. The deformation density in all C—C bonds is found to be elongated in a direction normal to the benzene ring, as a result of π bonding.

As a result of conjugation of the nitrogen p_π and sulfur d orbitals with the π system of the benzene ring, deviation from cylindrical symmetry of the bonding features can also be expected for the partial double C(4)—N and C(1)—S bonds. No significant deviations from cylindrical symmetry, however, can be found in either bond.

Fig. 4 shows the difference density in sections through the sulfate group. Bond peaks of about 0·30 eÅ^{-3} are found in the S—O bonds. In contrast to the sulfate group in sulfamic acid (Bats, Coppens & Koetzle, 1977) no lone-pair density is found around the sulfate O atoms, while the peak heights in the S—O bonds are somewhat lower in the present study. No lone-pair density was observed in sections through the hydrate O atoms either. A resolution higher than in the

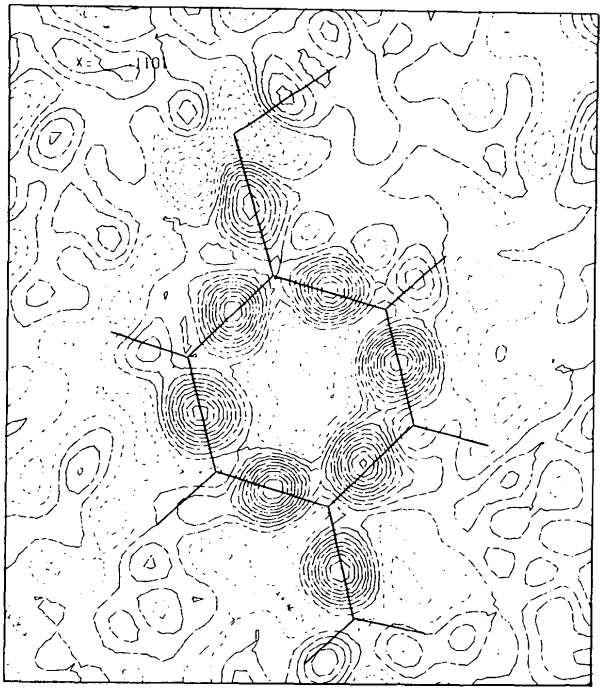

Fig. 2. Deformation density in the plane of the benzene ring with high-order atomic parameters. Data cut-off in Fourier synthesis: $\sin\theta/\lambda = 0{\cdot}75$ Å^{-1}. Contour interval 0·05 eÅ^{-3}. Negative contours are shown broken. Also shown are the amino group (bottom) and the S—O(2) bond (top).

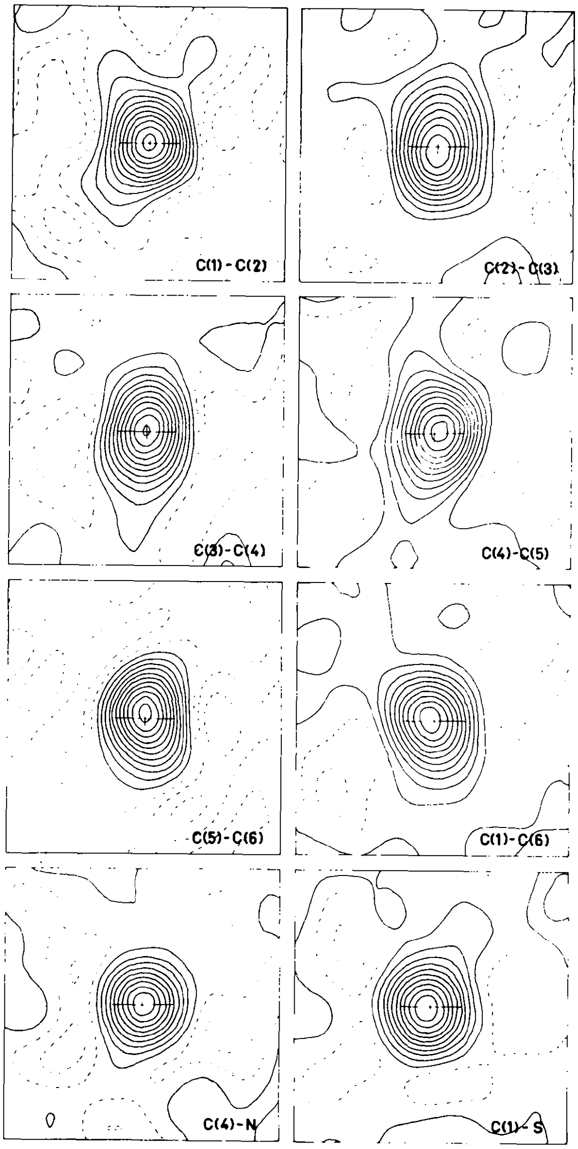

Fig. 3. Deformation density in cross-sections through the C—C, C—N and C—S bond peaks, normal to the bonds. The projection of the benzene ring is marked by a horizontal line. Contours as in Fig. 2.

present study is obviously needed to obtain atomic parameters for O unbiased by bonding effects.

Of interest is the N atom of the amino group, whose configuration in the room-temperature study was found to be closer to tetrahedral than planar, partly due to hydrogen bonding. Fig. 5 shows a difference density map through the N atom in a section perpendicular to the C(4)–N bond. A Newman projection of the amino group with respect to the plane of the benzene ring is included in this figure and reconfirms the non-planarity of the amino group. Clearly shown is lone-pair density at the apex of the CNH_2 pyramid. The O(5)″–H(9)″ ··· N hydrogen bond may be stronger than predicted previously (Bats & Coppens, 1975) as the O(5)″–H(9)″ bond points considerably more directly at the N lone-pair peak than towards the center of the N atom.

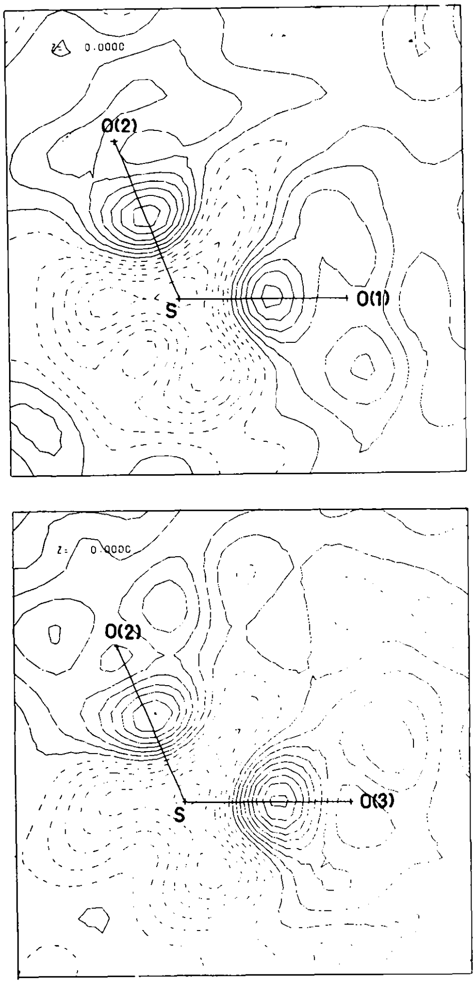

Fig. 4. Deformation density in sections through the sulfate group. Contours as in Fig. 2.

Charge-transfer analysis

In order to obtain insight into the charge transfer among the sulfanilate group, the Na atom and the hydrate molecules, the numerical integration procedure developed by Coppens (1975) has been applied to the present data set. In this method the space between atoms of different groups is divided according to the ratio of effective radii assigned to the atoms, which for the non-sodium atoms are taken as their van der Waals radii while for the Na atom a radius of 1·5 Å was used (Bats, Coppens & Kvick, 1977).

Net charges for the molecular fragments obtained in this way are reported in Table 9.

The sulfanilate group bears, as expected, a negative charge, though considerably smaller than that suggested by a pure ionic model. The Na atom is found to be almost neutral as in $NaCN.2H_2O$ (Bats, 1977). There is a charge transfer of about 0·15 e from both hydrate molecules towards the anion, in agreement with the net charge of +0·18 e averaged over four hydrate molecules by Coppens, Pautler & Griffin (1971) and the value of +0·23 e reported by Bats (1977) for the hydrate molecules in $NaCN.2H_2O$.

Table 9. *Net charge populations*

Group	Net charge	Volume of integration (Å^3)
Na	+0·07 (4)	17·8
Sulfanilate	−0·37 (4)	171·3
H_2O (I)	+0·14 (4)	23·0
H_2O (II)	+0·16 (4)	25·3

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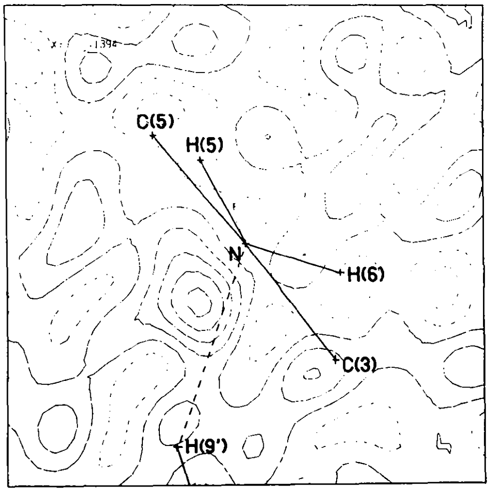

Fig. 5. Deformation density in a section through the N atom, normal to the C(4)–N axis. A Newman projection of the NH_2 group with respect to the plane of the benzene ring is included. Contours as in Fig. 2. The dotted line indicates the hydrogen bond.

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The Structure of a Cyclodimer from Reaction of 7-Methoxy-1,2-dihydronaphthalene with Sodium and Ethylenediamine. A Comparison of Bond Distances and Angles in Two Molecules

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6,6a,7,12,13,13a-Hexahydro-2,9-dimethoxy-7,13-methano-5*H*-benzo[4,5]cyclohepta[1,2-*a*]naphthalene, $C_{22}H_{24}O_2$, is a cyclodimerized product obtained from reaction of 7-methoxy-1,2-dihydronaphthalene with sodium and ethylenediamine. The preparation, isolation, and spectral data of this dimer are described. Crystals of the compound are monoclinic, space group $P2_1/c$. The cell dimensions are a = 26·643 (9), b = 8·165 (3), c = 16·226 (5) Å and β = 107·56 (2)°. The structure was determined by direct methods and refined with least-squares calculations on 6372 data collected at −160°C. The final R value is 0·060. The asymmetric unit contains two independent molecules which show good agreement of distances for corresponding bonds. It is concluded that the standard deviations calculated from the inverse of the least-squares matrix are not underestimated.

Introduction

The synthesis and crystallographic structure of 5,6,7,12,13,14-hexahydro-5,13:6,12-dimethanodibenzo[*a,f*]cyclodecane (I) were recently reported (Eisenbraun, Ansell, Dobbs, Harris, Hertzler, Ruehle, Burks & van der Helm, 1976) as a product obtained from reaction of naphthalene with sodium in ethylenediamine. Obtaining this unusual structure prompted extension of the reaction to 7-methoxy-1,2-dihydronaphthalene (II) in an effort to learn whether methoxylated dimers comparable to hydrocarbon I could be obtained. Dimers III, IV, and V are isolated as reaction products from treatment of II with sodium and ethylenediamine (Ansell, 1976). The mass spectral data of title compound V shows an *m/e* of 320, which strongly suggests a cyclodimer or an unsaturated monolinked dimer. The latter structural possibility is excluded by absence of vinyl proton signals in the ^{1}H NMR spectrum. Furthermore, the complexity of the ^{1}H NMR spectrum indicates lack of symmetry and a skeletal difference from symmetric dimers I and III which have simpler spectra. The complexity of the analytical data as well as the limited amount of