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X-ray and Neutron Diffraction Studies of β-Sulphanilamide

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The crystal structure of *β*-sulphanilamide has been refined from three-dimensional photographic X-ray data and two-dimensional neutron diffraction data. Positional and anisotropic thermal parameters of the non-hydrogen atoms and positional and isotropic thermal parameters of the hydrogen atoms were refined in the X-ray analysis to give a final *R* index of 4·9 %. Positional and isotropic thermal parameters of the hydrogen atoms were refined in the neutron study. The final residual factors were $R(h0l) = 8{\cdot}0\ \%$, $R(hk0) = 9{\cdot}1\ \%$. The mean standard deviation in the C–C bonds is 0·0028 Å and the e.s.d.'s in the hydrogen atom positional parameters are approximately 0·035 Å. The bond lengths suggest that there is a small but significant contribution of a quinonoid resonance form to the structure of the molecule. The distribution of residual electron density within the benzene ring and in the tetrahedral sulphamide group is explained in terms of effects resulting from electron redistribution at bonding. The hydrogen bond system closely resembles that found in α-sulphanilamide and the N–H···O bonds are about 0·25 Å longer than in related zwitterion compounds.

Introduction

The study of *β*-sulphanilamide ($NH_2.C_6H_4.SO_2NH_2$) forms part of a program of structure analysis of the anilinesulphonic acids and sulphonamides being pursued in this laboratory. The structures of sulphanilic acid monohydrate (Rae & Maslen, 1962), metanilic acid (Hall & Maslen, 1965), orthanilic acid (Hall, 1964) and α-sulphanilamide (O'Connor & Maslen, 1965) have been reported. The aim of this program is to obtain information about bond length variations in disubstituted benzenes and electron density distributions within the benzene ring and in the related charged and neutral groups, and to compare the hydrogen bond systems of the various compounds.

The *para* substituents of sulphanilamide make it an ideal structure for the study of benzene ring distortions as the equivalence of pairs of bonds provides a valuable check on the accuracy of structural parameters, since these are independent of crystal symmetry. In the present analysis it was hoped to obtain further information about the dumbell shaped peaks of residual density which appeared above and below the bonds of the planar part of the molecule in the final difference synthesis of orthanilic acid. A neutron diffraction analysis was carried out concurrently with the X-ray refinement to confirm the hydrogen atom parameters and also to provide evidence of the displacement of the electron density maxima from the nuclear positions (Stewart, Davidson & Simpson, 1965).

Four crystalline habits of sulphanilamide have been reported (Watanabe, 1941; Yakowitz, 1948; McLachlan, 1957). The structures of the α (O'Connor & Maslen, 1965) and the γ form (Alléaume & Decap, 1965*a*) are known. During the course of this analysis the results of a similar study of *β*-sulphanilamide (Alléaume & Decap, 1965*b*) became known to the authors. The present solution and refinement were carried out independently except that during part of the least-squares refinement the hydrogen parameters proposed by Alléaume & Decap were included. It was found, however, that some of these parameters were grossly in error. Positive identification of the hydrogen atom positions in the present analysis by both X-ray and neutron diffraction techniques provides an interesting example of the incorrect conclusions that can be deduced when data of limited accuracy are used in the structure refinement.

Crystal data

$C_6H_8N_2O_2S$, *p*-aminobenzenesulphonamide.
Monoclinic:
$a = 8{\cdot}975 \pm 0{\cdot}003$, $b = 9{\cdot}005 \pm 0{\cdot}003$,
$c = 10{\cdot}039 \pm 0{\cdot}004$ Å, $\beta = 111°26' \pm 3'$.
$U = 755{\cdot}2$ Å^3.
$Z = 4$; $D_m = 1{\cdot}520 \pm 0{\cdot}004$ g.cm^{-3} by flotation;
$D_x = 1{\cdot}514$ g.cm^{-3}.
Space group $P2_1/c$.
Absent spectra: 0*k*0, *k* odd; *h*0*l*, *l* odd.
$\mu = 32{\cdot}98$ cm^{-1} for $\lambda = 1{\cdot}5418$.

Experimental

X-ray data

Well formed crystals of the *β* type were obtained by controlled evaporation of a solution of sulphanilamide in aqueous alcohol at 38 °C. Two crystals, measuring $0{\cdot}128 \times 0{\cdot}176 \times 0{\cdot}440$ mm^3 and $0{\cdot}240 \times 0{\cdot}330 \times 0{\cdot}230$ mm^3, were selected for the intensity measurements. Multi-film and exposure equi-inclination Weissenberg techniques with Cu *Kα* radiation were employed to col-

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lect intensities on layers 0 to 7 and 0 to 9 for the *b* and *c* axes respectively. This represented all non-equivalent reciprocal lattice points within the copper sphere. Since both elongated and contracted spots were to be measured it was necessary to collect two sets of intensity films per layer at different angular settings of the crystal for the *c* axis data. For layers *hk*1 and *hk*2 this procedure was not adopted since the spot shape variation was not serious and did not affect the measurements significantly.

The data were estimated visually by comparison with standard scales. Intra-pack film factors were determined by measuring the absorption of Cu $K\alpha$ radiation in 'Ilfex' film by means of a scintillation counter detector. The ratio of incident to transmitted intensity of a reflected X-ray beam was measured for a large number of film samples, and a mean film factor $R_0 = 2{\cdot}95 \pm 0{\cdot}03$ was obtained for normal beam incidence. The appropriate angular corrections (Grenville-Wells, 1955) were applied to the non-zero layer film factors. During the collection of data the exposure times were adjusted so that interpack film factors were close to unity, enabling these scales to be obtained accurately from the ratio of intensities common to two packs.

The scale factor between the two sets of films on each of the layers *hk*3 to *hk*9 was determined from the ratio of common intensities in the two sets, with due regard to whether they were elongated or contracted reflexions. Lorentz, polarization and general absorption corrections similar to those described by Busing & Levy (1957) were applied to all reflexions. The interlayer correlation scales were obtained from the common rows of the two blocks of data. To guard against systematic errors of the type described by Rollett & Sparks (1960), which may be introduced by referring the scales to only one layer, the scaling process was repeated four times with different principal layers. No systematic differences between these sets were detected, the largest deviation between any scale and the corresponding mean layer scale being 1·2%.

Of the 1627 intensities measured 1478 were observable above background. The remainder were given values equal to the minimum observable and treated as unobserved reflexions as described below. The 'correlation *R*-factor', $R_c = 2\,\Sigma\,(||F_b| - |F_c||)/\Sigma\,(|F_b| + |F_c|)$, for the 1035 terms common to both sets was 0·056. This corresponds to a mean e.s.d. of 5·0% in the $|F_o|$'s (Ibers, 1956).

Neutron data

The neutron diffraction data were collected at the Australian Atomic Energy Commission's HIFAR reactor. Samples measuring $2{\cdot}3 \times 2{\cdot}3 \times 2{\cdot}3$ mm^3 and $2{\cdot}3 \times 2{\cdot}3 \times 5{\cdot}0$ mm^3 were mounted on vanadium strips on two goniometer heads. Intensities for 153 *h*0*l* and 158 *hk*0 reflexions having 2θ less than 110° ($\lambda = 0{\cdot}940$ Å) were recorded. Of these 106 *h*0*l* and 103 *hk*0 reflexions had intensities measurable above background. The data were reduced by applying the usual angular corrections. No corrections for extinction or absorption were necessary.

Structure solution and refinement

X-ray data

The solution and initial refinement were carried out with partial data only. Layers *hk*0 to *hk*4, scaled by Wilson's (1942) method, were employed in this part of the analysis. The structure solution was obtained by the heavy atom method. A three-dimensional sharpened Patterson synthesis was used to determine the sulphur atom coordinates and the remaining ten non-hydrogen atoms were positioned from a three-dimensional sulphur phased electron density Fourier synthesis.

After one cycle of difference synthesis refinement the *R* index was 0·28. The structure was refined by least-squares methods with Mair's (1962) program for the IBM 1620 computer. This program, which makes use of the block diagonal approximation, allows positional, isotropic or anisotropic parameters to be varied. The function $\Sigma\,\omega(|F_o| - |F_c|)^2$ is minimized. Throughout the refinement unobserved terms with $|F_o|$ greater than $|F_c|$ were given zero weight, while those with $|F_o|$ less than $|F_c|$ were treated as observed reflexions. This is similar to the treatment of unobservably weak reflexions suggested by Vand & Dunning (1965). The atomic scattering factors used were those of Hanson, Herman, Lea & Skillman (1964).

The real part of the anomalous dispersion coefficient (Cromer, 1965) was applied to the sulphur curve and the correction factor ($k = 2{\cdot}5$) suggested by Jensen & Sundaralingam (1965) was applied to the isolated atom hydrogen form factor. Reflexion weights were calculated according to the following three schemes:

Scheme I	$\vert F_o\vert > F^*$,	$\sqrt{\omega} = F^*/\vert F_o\vert$
	$\vert F_o\vert < F^*$,	$\sqrt{\omega} = \vert F_o\vert/F^*$
Scheme II	$\vert F_o\vert > F^*$	$\sqrt{\omega} = F^*/\vert F_o\vert$
	$\vert F_o\vert < F^*$	$\sqrt{\omega} = 1{\cdot}0$
Scheme III		$\sqrt{\omega} = 1/\Delta F_{bc}$

where F^* is chosen to be in the most reliable range of $|F_o|$ and ΔF_{bc} is the difference between the observed structure factors measured about the *b* and *c* axes. The calculation of weights according to scheme III was possible since a large number of reflexions (about 70%) were common to both sets of data. A plot of $1/\Delta F_{bc}$ against $|F_o|$ for these reflexions resulted in a smooth curve (Fig. 1) from which individual weights were assigned by interpolation. The population densities of the common reflexions and of all reflexions, plotted for ranges of $|F_o|$, are also shown on the graph.

During the initial stages of the analysis weights were calculated according to scheme I, F^* being chosen as 10 electrons. After three cycles of refinement of positional and isotropic temperature parameter the *R* index dropped to 0·14. The complete set of three-dimensional data was then introduced and the refinement was continued giving all non-hydrogen atoms anisotropic temperature coefficients, and including the hydrogen atom parameters reported by Alléaume & Decap (1965*b*). After six cycles of least squares R decreased to 0·080, a stationary value, and no significant shifts in the atomic parameters were indicated. Although the structure appeared to have been refined to the limit of accuracy of the data there were some large discrepancies between chemically equivalent bonds in the benzene ring, C(3)–C(4) and C(4)–C(5) differing by 0·06 Å, or about 10σ. This was attributed to the rather large weight given to high intensity terms which are subject to secondary extinction errors. In view of this the analysis was continued with scheme II, F^* being chosen as 2·5 electrons. Several rounds of refinement reduced R to 0·069, the maximum difference between chemically equivalent bonds being 2σ. Weighting scheme III was then introduced and after two rounds of least-squares the residual decreased to 0·067.

As a check on the hydrogen atom parameters of Alléaume & Decap a three-dimensional difference synthesis, phased only on the sulphur, carbon, nitrogen and oxygen atoms, was evaluated. The hydrogen atom positions determined by this method differed considerably from those of Alléaume & Decap. Fig. 2, a composite projection of this synthesis, shows seven of the eight hydrogen atoms with maximum peak densities between 0·6 and 0·8 e.Å^{-3}. The low peak height of the atom H(7), which is not involved in the intermolecular hydrogen bond system, was attributed to its large thermal motion perpendicular to the plane of the amino group. Structure factors were evaluated assuming isotropic thermal parameters with $B=3{\cdot}5$ Å^2 for the hydrogen atoms. The analysis R values at this stage of the analysis were:

R (no hydrogen) = 0·074.
R (hydrogen of Alléaume & Decap) = 0·065.
R (hydrogen from difference synthesis) = 0·062.

Two more least-squares refinement cycles of the non-hydrogen atoms produced no significant changes in the structure or the residual index.

Examination of the structure factors showed that for all large terms the calculated values were larger than the observed ones, indicating the presence of secondary extinction. An estimate of the secondary extinction coefficient was obtained from plots of I_o/I_c against I_c (James, 1948). Since the *b*- and *c*-axis data were collected from different crystals separate corrections were made to each set, the coefficients being 0·66 and $0{\cdot}83 \times 10^{-5}$ respectively. When the data were recorrelated as described above the agreement between observed and calculated values improved considerably and the residual index decreased to 0·052. After two more rounds of least-squares R fell to 0·051 and no significant changes in the parameters were recorded.

A series of refinement cycles on only the hydrogen atom positional and isotropic temperature parameters were then calculated. The shifts predicted were physically reasonable and the residual decreased to 0·050. A further two rounds of refinement on the non-hydro-

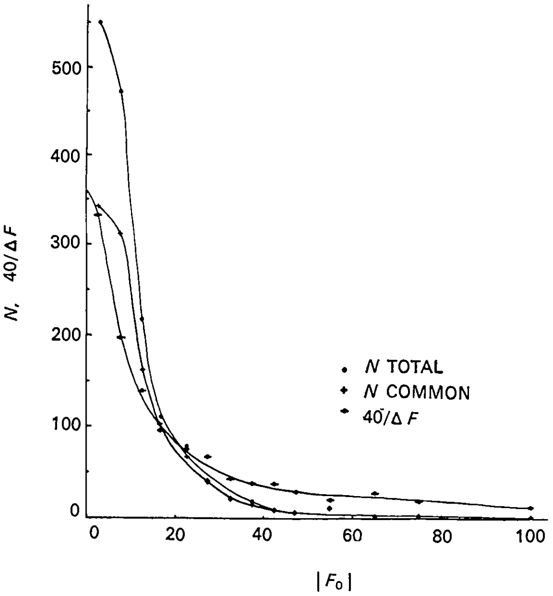

Fig. 1. Correlation agreement plot. The mean $1/(|F_b - F_c|)$ for ranges of $|F_o|$ is plotted against $|F_o|$. The number of common terms and the total number of terms in each range are also plotted against $|F_o|$.

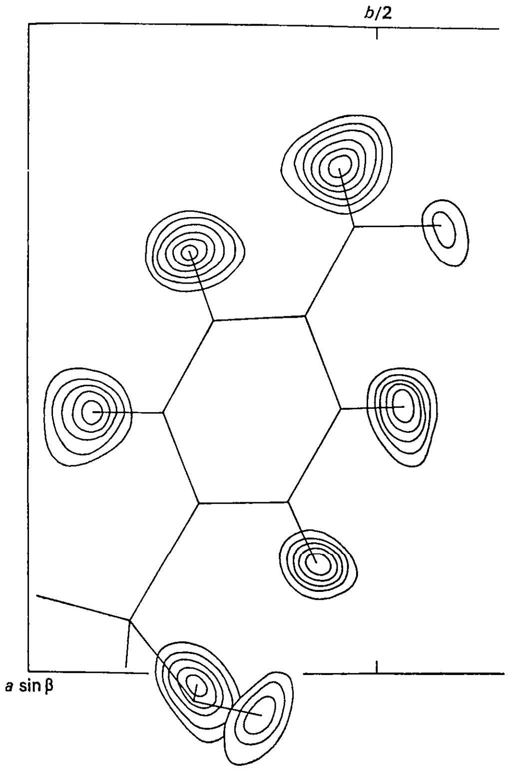

Fig. 2. A composite difference synthesis showing the hydrogen atoms. Contours are at intervals of 0·1 e.Å^{-3} from 0·2 e.Å^{-3}.

Table 1. *Observed and calculated structure factors*

H	K	L	10FO	10FC
0	0	2	700	-667
		4	191	-167
		6	64	-66
		8	20	22
		10	16	13
0	1	1	158	165
		2	761	-755
		3	94	96
		4	217	215
		5	259	-249
		6	385	-366
		7	79	74
		8	98	95
		9	16U	6
		10	15	-17
		11	16	16
0	2	0	243	-259
		1	297	324
		2	28	-14
		3	53	-60
		4	151	-140
		5	106	-86
		6	135	-136
		7	115	104
		8	123	122
		9	71	-69
		10	42	44
		11	88	58
0	3	1	45	37
		2	133	118
		3	11U	-12
		4	13U	7
		5	296	299
		6	37	-38
		7	342	-367
		8	221	222
		9	77	76
		10	80	-85
		11	8U	-8
0	4	0	21	-35
		1	447	-457
		2	356	368
		3	11U	14
		4	224	-215
		5	75	-80
		6	151	152
		7	47	45
		8	74	-74
		9	61	58
		10	66	-68
		11	27	-27
0	5	1	199	-193
		2	272	-256
		3	192	173
		4	104	-105
		5	108	109
		6	179	191
		7	65	-70
		8	167	-175
		9	11U	5
0	6	0	128	134
		1	138	-141
		2	142	-128
		3	108	102
		4	33	29
		5	41	-37
		6	105	-107
		7	45	-49
		8	21	24
		9	50	53
		10	35	42
0	7	1	45	-41
		2	11U	6
		3	113	109
		4	37	-40
		5	187	-185
		6	43	-38
		7	136	143
		8	83	80
		9	96	-97
0	8	0	251	262
		1	175	163
		2	122	-127
		3	75	-72
		4	45	-47
		5	30	29
		6	71	68
		7	19	-16
		8	17	21
0	9	1	16U	-1
		2	103	-106
		3	39	37
		4	136	142
		5	19	20
		6	108	-109
		7	40	-46
0	10	0	159	-164
		1	37	36
		2	157	155
		3	12	-18
		4	97	-96
		5	80	-79
0	11	1	25	-24
		2	9U	10
		3	51	-54
1	0	0	339	394
		2	493	-499
		4	549	-508
		6	376	346
		8	26	-18
		10	60	57
1	1	0	473	543
		1	447	-471
		2	288	-296
		3	75	-68
		4	540	535
		5	31	-38
		6	184	-188
		7	137	137
		8	60	61
		9	64	-64
		10	12U	-4
		11	16U	-8
1	0	-2	956	-940
		-4	123	145
		-6	63	55
		-8	85	86
		-10	12U	-3
		-12	20	-20
1	1	-2	585	-577
		-3	761	779
		-4	318	-309
		-5	233	-221
		-6	157	140
		-7	148	144
		-8	162	-151
		-9	173	-161
		-10	19	15
		-11	74	71
1	2	0	173	-176
		1	503	524
		2	266	254
		3	11	-13
		4	95	-52
		5	113	-109
		6	67	-58
		7	41	35
		8	14U	19
		9	43	-37
		10	12U	7
		11	93	99
		-1	1034	-1067
		-2	562	584
		-3	235	264
		-4	52	48
		-5	10U	15
		-6	68	75
		-7	200	196
		-8	66	-61
		-10	109	-105
		-11	92	-97
		-12	18	17
1	3	0	76	81
		1	210	-161
		2	61	46
		3	149	-146
		4	69	73
		5	335	341
		6	211	-210
		7	94	-92
		8	51	58
		9	19	19
		10	9U	-4
		11	32	30
		-1	218	-230
		-2	405	-421
		-3	192	186
		-4	320	313
		-5	227	229
		-6	160	154
		-7	263	-282
1	3	-8	33	26
		-9	168	198
		-10	18	-17
		-11	55	-56
1	4	0	239	-243
		1	78	-78
		2	205	193
		3	86	85
		4	229	-238
		5	133	122
		6	83	-80
		7	114	-108
		8	139	141
		9	15U	6
		10	60	-68
		-1	36	39
		-2	58	70
		-3	190	-180
		-4	215	-221
		-5	116	112
		-6	178	180
		-7	60	-57
		-8	30	-32
		-9	33	30
		-10	11U	-10
		-11	8U	4
1	5	0	206	-203
		1	186	-171
		2	20	23
		3	13	-8
		4	241	-229
		5	51	-44
		6	359	390
		7	55	-54
		8	142	-151
		9	14U	1
		10	41	47
		-1	122	112
		-2	95	95
		-3	105	106
		-4	10U	14
		-5	24	27
		-6	205	-212
		-7	113	-114
		-8	147	155
		-9	46	45
		-10	87	-87
		-11	15	-14
1	6	0	292	307
		1	242	-220
		2	57	-50
		3	25	-25
		4	36	35
		5	112	109
		6	13U	2
		7	19	-25
		8	9U	6
		9	72	75
		-1	87	81
		-2	222	-213
		-3	102	-101
		-4	64	59
		-5	127	122
		-6	55	-53
		-7	63	-65
		-8	87	85
		-9	20	20
		-10	9U	-9
1	7	0	16	-13
		1	121	-127
		2	16	14
		3	120	121
		4	12U	-2
		5	75	-74
		6	11U	5
		7	115	114
		8	9U	4
		9	16	-18
		-1	91	98
		-2	43	43
		-3	29	32
		-4	12U	6
		-5	131	-141
		-6	33	-39
		-7	138	135
		-8	11U	12
		-9	83	-93
1	8	0	205	195
		1	116	121
		2	63	-59
		3	59	-56
		4	94	-96
		5	12U	14
		6	16U	21
		7	23	26
		-1	202	-193
		-2	171	-164
		-3	154	160
		-4	51	60
		-5	74	-66
		-6	17U	14
		-7	76	69
		-8	26	-29
1	9	0	114	100
		1	55	-56
		2	195	-197
		3	51	-50
		4	121	123
		5	113	114
		6	58	-59
		7	64	-77
		-1	58	-58
		-2	59	-51
		-3	31	34
		-4	44	-47
		-5	37	38
		-6	100	101
		-7	56	-57
1	10	0	137	-122
		1	41	40
		2	56	54
		3	66	63
		4	63	61
		-1	98	-94
		-2	101	95
		-3	12U	-11
		-4	94	-97
		-5	8U	7
		-6	61	70
1	11	0	32	-37
		1	33	35
		2	68	67
		3	24	-30
		-1	19	21
		-2	9U	4
		-3	9U	-6
2	0	0	543	664
		2	302	266
		4	250	-242
		6	106	108
		8	101	-93
		10	104	105
2	1	0	194	206
		1	468	-457
		2	257	-268
		3	261	252
		4	81	100
		5	66	-53
		6	179	-179
		7	103	102
		8	59	62
		9	13U	-11
		10	19	18
2	0	-2	409	-431
		-4	74	-62
		-6	91	87
		-8	174	185
		-10	98	-104
		-12	140	-138
2	1	-1	416	451
		-2	37	-37
		-3	532	-527
		-4	171	171
		-5	90	-92
		-6	206	198
		-7	150	151
		-8	63	-56
		-9	13U	9
		-10	148	141
		-11	32	30
		-12	98	-95
2	2	0	358	-347
		1	508	518
		2	167	153
		3	102	90
		4	123	110
		5	243	-241
		6	118	-111
		7	109	112
		8	49	53
		9	77	-78
2	2	10	39	-38
		-1	373	-384
		-2	588	-619
		-3	417	447
		-4	71	-73
		-5	410	-441
		-6	289	279
		-7	233	244
		-8	64	-58
		-9	160	-186
		-10	80	78
		-11	84	88
		-12	21	17
2	3	0	260	259
		1	91	-68
		2	15	-17
		3	279	-273
		4	11U	7
		5	274	276
		6	22	-24
		7	132	-126
		8	40	48
		9	34	-31
		10	25	28
		-1	275	-288
		-2	166	-171
		-3	348	353
		-4	362	-376
		-5	114	117
		-6	43	46
		-7	176	-173
		-8	129	-127
		-9	120	119
		-10	41	41
		-11	76	-82
		-12	14	14
2	4	0	206	-201
		1	240	-214
		2	88	78
		3	31	22
		4	320	339
		5	60	48
		6	187	-189
		7	14U	11
		8	108	114
		9	44	46
		10	79	-91
		-1	108	111
		-2	97	105
		-3	124	-131
		-4	44	-49
		-5	47	43
		-6	169	168
		-7	78	-67
		-8	118	-117
		-9	78	71
		-10	50	-48
		-11	30	27
2	5	0	238	-232
		1	101	-99
		2	300	295
		3	75	66
		4	204	-211
		5	170	176
		6	94	87
		7	19	38
		8	55	-59
		9	41	-45
		-1	88	-78
		-2	383	373
		-3	103	107
		-4	77	-78
		-5	48	-45
		-6	143	-140
		-7	79	-81
		-8	156	159
		-9	29	29
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		-4	127	138
		-5	18	20
		-6	71	-79
7	0	0	78	80
		2	168	-162
		4	65	-66
		6	59	-53
7	1	0	287	-298
		1	65	63
		2	92	90
		3	102	-98
		4	114	-114
		5	22	21
		6	40	40
7	0	-2	466	516
		-4	268	-284
		-6	42	39
		-8	64	63
		-10	49	-48
		-12	29	27
7	1	-1	87	83
		-2	23	26
		-3	97	-94
		-4	128	126
		-5	115	115
		-6	79	-77
		-7	175	-182
		-8	134	139
		-9	111	109
		-10	60	-58
		-11	48	-44
		-12	38	33
7	2	0	71	68
7	2	1	147	-149
		2	37	-34
		3	92	88
		4	13U	-1
		5	27	-27
		6	27	26
		-1	208	207
		-2	90	-91
		-3	216	-231
		-4	44	47
		-5	211	217
		-6	145	-138
		-7	93	-82
		-8	64	-66
		-9	66	-71
		-10	90	83
		-11	47	51
		-12	19	-18
7	3	0	16U	9
		1	110	-110
		2	83	78
		3	130	125
		4	58	-55
		5	58	-90
		6	86	84
		-1	15U	-10
		-2	33	33
		-3	116	116
		-4	16	13
		-5	23	-27
		-6	62	58
		-7	84	86
		-8	98	-93
		-9	190	-194
		-10	61	-61
		-11	76	77
7	4	0	112	104
		1	25	-29
		2	121	-118
		3	27	-23
		4	31	29
		5	12	12
		-1	88	-92
		-2	25	-19
		-3	152	156
		-4	118	114
		-5	44	-43
		-6	30	-32
		-7	58	53
		-8	14	13
		-9	21	-21
		-10	9U	9
7	5	0	47	-50
		1	27	29
		2	153	-159
		3	61	61
		4	124	132
		-1	98	-102
		-2	93	80
		-3	11U	6
		-4	36	-34
		-5	60	59
		-6	53	52
		-7	33	31
		-8	91	-90
		-9	50	-52
		-10	103	107
7	6	0	93	-89
		1	67	61
		3	44	-42
		4	52	-56
		-1	78	-75
		-2	93	88
		-3	102	92
		-4	71	-68
		-5	118	-119
		-6	25	22
		-7	69	71
		-8	35	-33
		-9	15U	-15
7	7	0	20	18
		1	62	65
		2	7U	-4
		3	73	-61
		-1	19	-18
		-2	28	-25
		-3	39	-39
		-4	16	17
		-5	69	63
		-6	53	49
		-7	83	-82
		-8	6U	6
		-9	61	66
7	8	1	42	-51
		-1	91	86
		-2	97	89
		-3	98	-96
		-4	97	-98
		-5	78	75
7	9	-3	33	37
		-4	28	32
8	0	0	62	-58
		2	26	-29
		4	62	54
8	1	0	17U	-12
		1	82	76
		2	157	154
		3	90	-87
		4	28	-35
		5	71	74
8	0	-2	68	63
		-4	237	-238
		-6	106	109
		-8	13U	-9
		-10	53	-46
8	1	-1	202	-201
		-2	32	36
		-3	114	113
		-4	15U	3
		-6	64	-59
		-7	15U	-10
		-8	70	70
		-9	16U	11
		-10	145	-134
		-11	78	-77
8	2	0	18U	4
		1	15U	5
		2	22	-20
		3	23	21
		4	31	-29
		5	16	19
		-1	83	77
		-2	16U	-9
		-3	285	-303
		-4	124	125
		-5	218	220
		-6	20	18
		-7	64	-64
		-8	68	69
		-9	82	84
		-10	68	-61
		-11	50	-52
8	3	0	21	-20
		1	150	-141
		2	33	34
		3	153	152
		4	41	-44
		-1	37	34
		-2	104	-106
		-3	12U	-7
		-4	14U	-4
		-5	29	28
		-6	16	15
		-7	24	28
		-8	115	117
		-9	83	-89
		-10	33	-34
		-11	79	86
8	4	0	42	43
		1	58	59
		2	18	-17
		3	9U	-5
		4	47	-47
		-1	51	-48
		-2	106	-103
		-3	47	47
		-4	76	71
		-5	62	-62
		-6	119	-117
		-7	46	42
		-8	50	47
		-9	14U	2
8	5	0	99	98
		1	55	-54
		2	113	-113
		-1	9U	-4
		-2	45	-40
		-3	10U	8
		-4	12U	7
		-6	43	40
8	5	-6	22	24
		-7	17	-20
		-8	85	-86
		-9	11U	-6
		-10	88	101
8	6	0	14U	-5
		1	16	17
		-1	83	-85
		-2	95	97
		-3	87	78
		-4	128	-125
		-5	89	-84
		-6	76	74
		-7	55	54
8	7	0	23	-28
		1	75	87
		-1	62	-60
		-2	9U	9
		-3	36	34
		-4	25	20
		-5	19	16
		-6	22	-23
		-7	45	-44
8	8	-1	35	40
		-2	17	18
		-3	82	-95
		-4	55	-56
		-5	87	98
9	0	0	14	15
		2	11U	-5
9	1	0	119	-114
		1	91	81
		2	77	73
		3	24	-27
9	0	-2	145	148
		-4	237	-221
		-6	162	169
		-8	20	-21
		-10	122	113
9	1	-1	41	-42
		-2	19	17
		-3	35	32
		-4	15U	-15
		-5	97	-91
		-6	19	18
		-7	14U	8
		-8	25	25
		-9	58	59
9	2	0	59	51
		1	59	57
		2	20	22
		3	79	-82
		-1	32	29
		-2	91	-90
		-3	37	-37
		-4	106	-106
		-5	100	95
		-6	22	16
		-7	95	-95
		-8	12U	13
		-9	28	31
		-10	19	-16
9	3	0	17U	-12
		1	160	-160
		2	32	28
		3	100	108
		-1	66	63
		-2	124	122
		-3	80	-76
		-4	73	-68
		-5	95	90
		-6	53	-50
		-7	13U	-11
		-8	25	26
		-9	37	-40
		-10	68	-74
9	4	0	13U	-8
		1	8U	4
		2	65	65
		-1	37	-34
		-2	70	-65
		-3	48	58
		-4	141	151
		-5	106	-103
		-6	102	-105
		-7	44	43
		-8	103	101
		-9	39	-40
9	5	0	77	76
		-1	8U	1
		-2	63	-64
		-3	9U	-3
		-4	72	69
		-5	31	27
		-6	28	-29
		-7	25	-26
		-8	49	-48
		-9	26	-27
9	6	-1	17	16
		-2	16	-13
		-3	55	55
		-4	99	-98
		-5	78	-77
		-6	107	109
		-7	66	68
9	7	-2	31	33
		-3	80	89
		-4	64	-64
		-5	55	-55
10	0	0	45	44
10	1	0	94	-93
		1	18	17
10	0	-2	40	36
		-4	89	-82
		-6	26	22
		-8	78	-83
		-10	55	55
10	1	-1	35	-30
		-2	70	69
		-3	86	83
		-4	43	-41
		-5	53	-50
		-6	62	62
		-7	30	-27
		-8	59	-56
		-9	28	28
10	2	0	62	54
		1	77	83
		-1	50	-48
		-2	51	-51
		-3	75	-73
		-4	62	62
		-5	82	87
		-6	19	20
		-7	54	-57
		-8	11U	-12
		-9	46	53
10	3	0	10	-11
		1	28	-35
		-1	104	106
		-2	40	37
		-3	31	-36
		-4	90	-91
		-5	34	36
		-6	104	107
		-7	79	-80
		-8	9U	5
10	4	0	41	-40
		-1	22	21
		-2	9U	-1
		-3	32	31
		-4	21	19
		-5	26	26
		-6	106	-114
		-7	25	25
		-8	88	102
10	5	-1	4U	-1
		-2	75	-79
		-3	9	-10
		-4	119	123
		-5	13	-13
		-6	92	-104
11	0	-2	34	-34
		-4	14	-10
		-6	56	56
11	1	-2	67	69
		-3	62	62
		-4	69	-70
		-5	76	-76
		-6	57	56
		-7	56	61
11	2	-3	16	16
		-4	19	20
		-5	36	36
		-6	12	11
		-7	34	-46
11	3	-3	35	-44
		-4	44	-45
		-5	67	76
		-6	20	29

gen atoms reduced R to 0·049 and no further parameter shifts were indicated. The final set of observed and calculated structure factors is listed in Table 1.

An attempt to minimize the effect of bonding electron asphericity on the parameters of the structure by a refinement using only those terms with sin θ/λ greater than 0·4 Å^{-1} proved unsuccessful because of an erroneously large scale shift given by the least-squares calculations. No explanation for these results can be suggested, especially as a shift of similar magnitude, but opposite sign, has been noted in the refinement of the structure of orthanilic acid. Further examination of structure refinements using upper angle terms, preferably with data measured by counting techniques so that scaling errors are minimized, is clearly desirable.

Neutron data

A set of structure factors was evaluated from the final positional and thermal parameters of the X-ray refinement and the neutron scattering lengths of Bacon (1962) for hydrogen, sulphur, carbon, nitrogen and oxygen. An examination of the agreement between observed and calculated values indicated that an overall temperature factor correction should be applied to the data. Similar discrepancies between X-ray and neutron diffraction results have been observed by Rietveld (1963). The accuracy of the present two-dimensional data does not allow a rigorous analysis of the differences in the two diffraction techniques, but it is interesting to note that the decrease in overall temperature factor is in accord with recent theoretical predictions. It has been shown (O'Connell, Rae & Maslen, 1965) that the aspherical electron density distribution in benzene results in the X-ray method predicting erroneously high thermal parameters for the carbon atoms in this structure.

Using Wilson's (1942) method corrections $\Delta B = -1{\cdot}0$ and $\Delta B = -0{\cdot}76$ were calculated for the $h0l$ and $hk0$ zones respectively. After applying these corrections the structural factor residuals were:

$$R\,(h0l) = 0{\cdot}19$$
$$R\,(hk0) = 0{\cdot}17$$

Figs. 3 and 4 are difference syntheses calculated from sets of structure factors phased only on the heavy atom parameters. The positions for all hydrogen atoms are clearly defined and are near the sites predicted from the three-dimensional X-ray analysis.

The least-squares refinement was carried out with weights calculated according to the scheme:

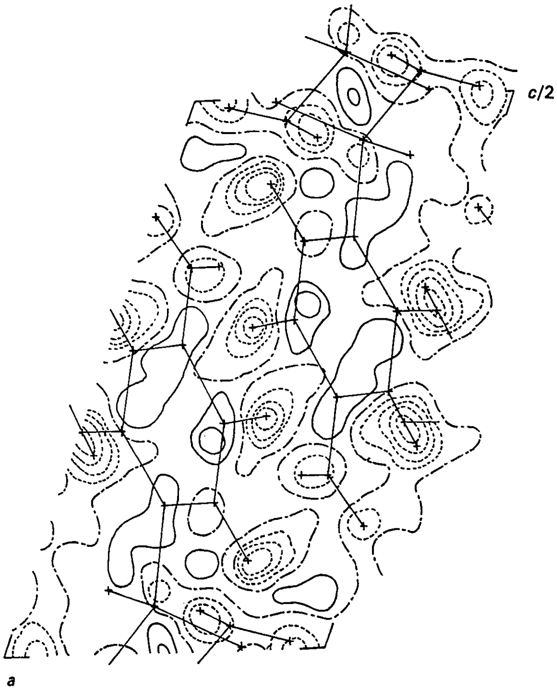

Fig. 3. [010] neutron diffraction difference synthesis, hydrogen atom contribution omitted. Zero countour chain-dotted, negative contour dashed, positive contours full line; in intervals of 0·2 × 10^{-12} cm.Å^{-2}.

Table 2. *Observed and calculated structure factors for the* (*h*0*l*) *zone*

H	K	L	FO	FC	H	K	L	FO	10FC	H	K	L	FO	FC
0	2	0	384	-410	1	10	0	106U	-161	2	14	0	74U	48
	4		480	488		11		71U	-85		15		105U	164
	6		74U	92		12		120U	136	3	0		429	364
	8		673	750		13		74	-70		1		400	-389
	10		290	-245		14		109U	151		2		180	192
	12		72U	-1	2	0		400	469		3		435	450
	14		96	-102		1		221	-161		4		109	-106
	16		130U	159		2		229	-233		5		146	-137
1	0		250	-261		3		415	427		6		142	138
	1		461	501		4		117	-116		7		1013	1125
	2		91	63		5		252	-245		8		64U	-53
	3		314	-326		7		97	-45		9		286	-241
	4		60	56		8		101U	-96		10		248	-238
	5		209	-116		9		228	210		11		94U	117
	6		192	209		10		69U	43		12		92U	-84
	7		60U	6		11		100U	114		13		132U	-131
	8		396	395		12		87	99		14		105U	-94
	9		260	235		13		131U	119	4	0		547	582

H	K	L	FO	FC	H	K	L	FO	10FC	H	K	L	FO	FC
4	1	0	244	221	5	4	0	311	-323	6	8	0	135	-89
	2		624	-599		5		287	-262		9		179	-188
	3		156	-139		6		64U	13		11		114	81
	4		291	-212		7		254	266	7	0		717	728
	5		660	-634		8		402	-374		1		845	-933
	6		576	-554		9		69U	78		2		63U	1
	7		599	-643		10		71U	48		3		64U	51
	8		495	549		11		54	-68		4		64U	45
	9		68U	63		12		73U	-70		5		637	-542
	10		268	-279		13		113	-113		6		123	-42
	11		72U	43	6	0		982	-999		7		115	98
	12		73U	43		1		227	200		8		139	117
	13		74U	67		2		401	438		9		280	-307
	14		52U	-101		3		467	442		10		73U	-49
5	0		289	-274		4		67U	-80		11		73U	13
	1		141	-130		5		188	149		12		74U	-72
	2		479	-454		6		281	270		13		100	-103
	3		548	515		7		207	199					

H	K	L	FO	FC	H	K	L	FO	10FC	H	K	L	FO	FC
8	0	0	64U	-72	9	5	0	70U	-19	11	2	0	72U	-138
	1		192	177		6		71U	117		3		73U	92
	2		65U	-67		7		72U	-20		4		278	-281
	3		64U	35		8		73U	107		5		140	-163
	4		143	-128		9		138	128		6		131	-130
	5		68U	-36	10	0		70U	-40		7		74U	81
	6		173	167		1		185	-175		8		213	223
	7		71U	-27		2		353	344		9		142	-128
	8		88	80		3		109	114	12	0		73U	-91
	9		73U	-30		4		71U	-37		1		92	68
	10		73U	-30		5		141	74		2		73U	36
	11		65	60		6		363	366		3		73U	20
9	0		68U	-64		7		111	118		4		163	-169
	1		179	-130		8		272	-285		5		85	77
	2		319	296		9		126	-159		6		114	136
	3		114	97	11	0		121	132	13	1		268	227
	4		159	-165		1		137	-141	14	0		237	-207

Table 3. *Observed and calculated structure factors for the* (*hk*0) *zone*

H	K	L	FO	FC	H	K	L	FO	10FC	H	K	L	FO	FC
0	0	2	533	-554	1	0	-12	294	250	3	0	2	509	-454
		4	807	-844			-14	105	126			4	268	-252
		6	439	-442	2	0	0	412	448			6	446	395
		8	130	89			2	641	643			8	642	-649
		10	315	-289			4	211	-188			10	137U	41
		12	97U	29			6	290	279			12	100U	-7
1	0	2	149	-117			8	311	281			-2	418	-415
		4	957	-1085			10	95U	100			-4	425	-359
		6	836	886			12	162	-179			-6	410	-388
		8	401	385			-2	48U	26			-8	853	831
		10	203	-157			-4	832	-827			-10	175U	-179
		12	98U	-71			-6	803	749			-12	759	780
		-2	674	-702			-8	156U	157			-14	166	134
		-4	406	383			-10	277	-263	4	0	0	803	836
		-6	585	528			-12	740	-769			2	557	-557
		-8	248	273			-14	280	287			4	80U	-63
		-10	90U	-81	3	0	0	348	369			6	214	248

H	K	L	FO	FC	H	K	L	FO	10FC	H	K	L	FO	FC
4	0	8	307	320	5	0	-4	182	-173	6	0	-12	214	-219
		10	98U	27			-6	495	-538			-14	216	243
		12	229	274			-8	333	341	7	0	0	819	768
		-2	147	-117			-10	90U	-35			2	837	-882
		-4	109U	-121			-12	263	-250			4	92U	-117
		-6	558	574			-14	164U	171			6	316	-251
		-8	141	116	6	0	0	660	-642			8	131U	129
		-10	610	-659			2	283	319			10	105	-79
		-12	96U	17			4	394	382			-2	1023	1184
5	0	0	298	-306			6	259	280			-4	180	-129
		2	558	-574			8	98U	-196			-6	96U	-103
		4	267	-271			10	208	202			-8	322	284
		6	262	335			-2	308	312			-10	92U	3
		8	291	-266			-4	928	-1061			-12	97U	-124
		10	294	-242			-6	276	-239	8	0	0	84U	-67
		12	153U	-119			-8	828	865			2	205	-204
		-2	163	186			-10	91U	84			4	191	200

H	K	L	FO	FC	H	K	L	FO	10FC	H	K	L	FO	FC
8	0	6	394	380	9	0	-8	399	342	11	0	-6	97U	172
		8	100U	85			-10	566	622			-8	284	330
		10	99U	-132			-12	646	-693			-10	135	-180
		-2	618	-607	10	0	0	96U	-50			-12	100U	-139
		-4	196	-181			2	98U	-122	12	0	0	116	-109
		-6	170	-164			4	99U	96			2	100U	-175
		-8	357	308			6	173U	-121			-2	160	-194
		-10	326	-352			-2	234	255			-4	259	262
		-12	98	103			-4	255	-255			-6	98U	-48
9	0	0	92U	-30			-6	421	-436			-8	99U	-32
		2	95U	125			-8	75U	-102			-10	249	327
		4	253	-197			-10	97U	-94	13	0	0	97U	5
		6	100	-111			-12	126U	-17			-2	100U	89
		8	143	120			-14	396	472			-4	100U	-58
		-2	410	358	11	0	0	151	138			-6	419	-444
		-4	551	-598			-2	125U	63	14	0	0	240	-238
		-6	396	322			-4	134U	-118			-2	231	256

$$\omega=\frac{1}{\left[1+\frac{(F_o-b)^2}{a}\right]^{\frac{1}{2}}},$$

the constants a and b being determined from plots of $\sqrt{\{(|F_o|-|F_c|)^2-1\}}$ against $|F_o|$. Most rapid convergence was obtained by applying a relaxation factor of 0·5 to all shifts. After a series of refinement cycles, during which only the hydrogen atom positional and isotropic temperature parameters were varied, the structure factor residuals decreased to

$$R\,(h0l)=0{\cdot}080$$
$$R\,(hk0)=0{\cdot}091$$

and no further shifts were indicated. Difference syntheses indicated possible anisotropic motion for some of the hydrogen atoms, but the introduction of additional parameters was not justified in view of the limited amount of data and the overlap in both projections.

The final sets of structure factors are listed in Tables 2 and 3 for the $(h0l)$ and $(hk0)$ zones respectively.

Discussion

Accuracy

The final agreement index, $R=0{\cdot}049$, compares well with the good correlation, $R_c=0{\cdot}052$, obtained between the b- and c-axis data. The final parameters, with standard deviations estimated from the diagonal elements of the inverse to the normal equations matrix, are listed in Tables 4, 5 and 6 for the X-ray refinement and Table 7 for the neutron diffraction analysis. The e.s.d. in the electron density is 0·08 e.Å^{-3}.

Table 4. *Non-hydrogen atom atomic coordinates and (in parentheses) their standard deviations*

	x/a	y/b	z/c
S	0·08243 (4)	0·85326 (4)	0·28753 (4)
O(1)	0·00713 (17)	0·86047 (16)	0·13418 (15)
O(2)	0·11695 (17)	0·98978 (14)	0·36595 (17)
N(1)	−0·03952 (20)	0·76159 (19)	0·34060 (19)
N(2)	0·69212 (19)	0·53272 (22)	0·41005 (19)
C(1)	0·26272 (19)	0·75661 (19)	0·32723 (17)
C(2)	0·26607 (21)	0·62849 (19)	0·25025 (18)
C(3)	0·40872 (22)	0·55368 (21)	0·28011 (18)
C(4)	0·55062 (20)	0·60579 (22)	0·38458 (18)
C(5)	0·54441 (21)	0·73402 (22)	0·46142 (19)
C(6)	0·40144 (21)	0·80837 (20)	0·43327 (19)

Table 5. *Non-hydrogen atom thermal parameters* and (in parentheses) their standard deviations*

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
S	0·01003 (6)	0·00764 (5)	0·00865 (4)	0·00213 (6)	0·00658 (8)	0·00118 (6)
O(1)	0·01308 (20)	0·01424 (21)	0·00890 (15)	0·00542 (25)	0·00557 (28)	0·00442 (30)
O(2)	0·01448 (21)	0·00826 (15)	0·01504 (19)	−0·00212 (27)	0·00962 (33)	0·00144 (29)
N(1)	0·01308 (22)	0·01154 (21)	0·01243 (20)	0·00253 (34)	0·01244 (36)	−0·00136 (36)
N(2)	0·01067 (22)	0·01551 (26)	0·01338 (23)	0·00143 (38)	0·00839 (36)	0·00439 (39)
C(1)	0·00975 (20)	0·00799 (18)	0·00828 (17)	0·00158 (29)	0·00605 (31)	−0·00048 (32)
C(2)	0·01083 (23)	0·00958 (21)	0·00808 (18)	−0·00087 (30)	0·00501 (34)	−0·00083 (34)
C(3)	0·01262 (25)	0·00943 (21)	0·00897 (19)	−0·00092 (32)	0·00856 (35)	0·00161 (37)
C(4)	0·01022 (22)	0·01053 (21)	0·00888 (18)	0·00350 (34)	0·00819 (33)	0·00199 (38)
C(5)	0·01074 (24)	0·01053 (22)	0·00978 (20)	−0·00027 (35)	0·00400 (37)	−0·00231 (38)
C(6)	0·01183 (24)	0·00899 (21)	0·00921 (19)	−0·00138 (33)	0·00563 (36)	−0·00131 (38)

* The temperature factors are expressed in the form exp $[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{13}hl+b_{12}hk)]$

Table 6. *X-ray hydrogen atom parameters and (in parentheses) their standard deviations*

	x/a	y/b	z/c	B†	δ*
H(1)	0·1722 (28)	0·5856 (29)	0·1878 (25)	3·2	0·065 Å
H(2)	0·4108 (34)	0·4615 (35)	0·2290 (32)	4·2	0·122
H(3)	0·6502 (36)	0·7707 (35)	0·5274 (34)	4·4	0·197
H(4)	0·4011 (44)	0·9095 (37)	0·4822 (36)	5·3	0·081
H(5)	−0·0151 (36)	0·7578 (34)	0·4342 (32)	4·3	0·266
H(6)	−0·0628 (50)	0·6661 (46)	0·3197 (47)	6·4	0·500
H(7)	0·6924 (56)	0·4108 (61)	0·3974 (48)	9·1	0·872
H(8)	0·7816 (38)	0·5547 (35)	0·4800 (33)	4·9	0·233

* δ is the difference between the coordinates listed here and those reported by Alléaume & Decap.
† The temperature factors are expressed in the form exp $[-(B\sin^2\theta/\lambda^2)]$.

Table 7. *Neutron diffraction hydrogen atom parameters and (in parentheses) their standard deviations*

	[010] projection			[001] projection		
	x/a	z/c	B	x/a	y/b	B
H(1)	0·1553 (29)	0·1665 (25)	3·5	0·1537 (46)	0·5894 (42)	4·7
H(2)	0·4148 (34)	0·2188 (31)	4·6	0·4173 (46)	0·4550 (42)	4·5
H(3)	0·6497 (36)	0·5343 (33)	4·7	0·6543 (27)	0·7722 (28)	3·2
H(4)	0·4007 (46)	0·4934 (43)	6·1	0·4002 (57)	0·9067 (52)	6·1
H(5)	−0·0086 (36)	0·4467 (32)	4·7	−0·0067 (39)	0·7648 (70)	5·4
H(6)	−0·0770 (39)	0·2871 (36)	5·1	−0·0778 (60)	0·6671 (55)	6·6
H(7)	0·6877 (40)	0·3692 (36)	5·1	0·6984 (54)	0·4274 (47)	5·2
H(8)	0·7856 (36)	0·4943 (33)	4·7	0·7819 (43)	0·5585 (40)	4·1

There are no significant differences between the atomic positions of the non-hydrogen atoms of the present analysis and that of Alléaume & Decap (1965*b*). However, there are some large discrepancies between the proposed hydrogen atom coordinates of the two refinements. These are listed in Table 6. The confirmation of the present results by neutron diffraction methods illustrates the limited value of low accuracy refinements ($R=0{\cdot}11$ for Alléaume Decap's analysis) for the determination of hydrogen atom parameters.

Thermal motion

The anisotropic thermal parameters were transformed to obtain the axes of the ellipsoids of vibration and their direction cosines relative to the orthogonal system a^*, b, c. These results are given in Table 8. The vibrations are represented diagrammatically in Fig. 5, where the axes of the ellipsoids are proportional to the mean square amplitude. The *para* substituents have vibrations which are largely independent of those of the benzene ring. The sulphamide group appears to oscillate about the long axis of the molecule while the amino nitrogen has almost equal vibrational modes in and perpendicular to the plane of the molecule at right angles to the C–N bond. The vibrations of the carbon atoms of the benzene ring are more nearly isotropic than those of the substituent groups. An attempt was made to analyse the planar part of the molecule for rigid body oscillations (Cruickshank, 1965), but no evidence for this type of motion could be found. The bond lengths of the substituent groups were corrected for thermal motion effects (Busing & Levy, 1964) assuming that the nitrogen and oxygen atoms of the sulphamide group ride on the sulphur atom and that the amino nitrogen rides on C(4). The corrections were 0·016, 0·015, 0·017, and 0·011 Å for the C(4)–N(2), S–O(1), S–O(2) and S–N(1) bonds respectively.

Least-squares plane

The equation of the least-squares plane through the six carbon atoms, referred to the orthogonal system a, b, c^*, and the deviations of the approximately planar atoms of the molecule from it are given in Table 9. The benzene ring is significantly distorted from the planar configuration, the magnitudes of the deviations being similar to those found with *p*-nitroaniline (Trueblood, Goldish & Donohue, 1961). Both the amino nitrogen and the sulphur atoms are significantly out of the ring plane by about 0·04 Å in the same direction. The amino group is not pyramidal in the form required for sp^3 hybridization, although one hydrogen atom [H(7)] is displaced by 0·47 Å from the molecular plane, indicating that the configuration is not purely trigonal.

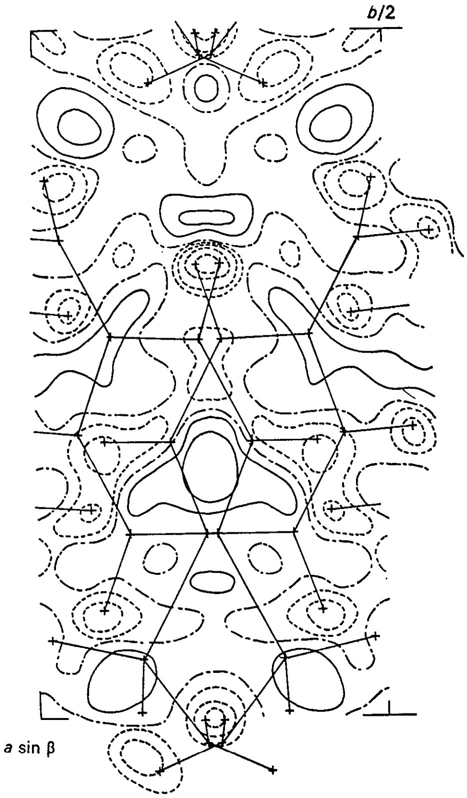

Fig. 4. [001] neutron diffraction difference synthesis, hydrogen atom contribution omitted. Zero contour chain dotted, negative contours dashed, positive contours full lines; at intervals of 0·2 × 10^{-12} cm.Å^{-2}.

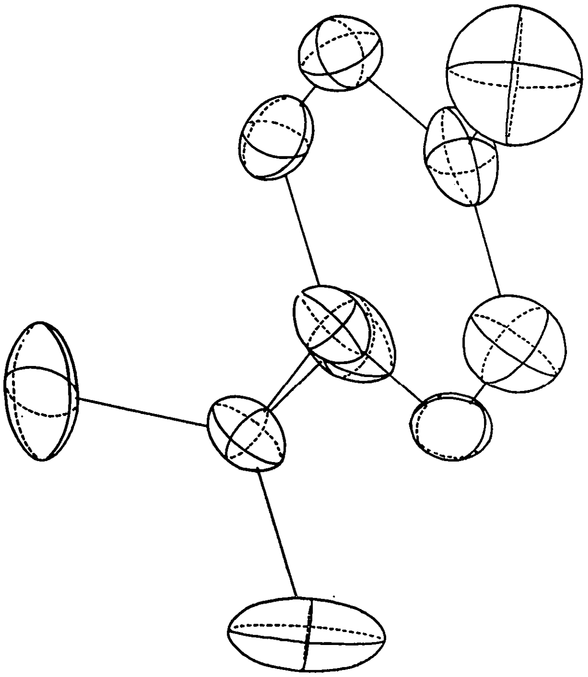

Fig. 5. The mean square vibrational displacements projected onto the (100) plane.

Bond lengths and angles

The intramolecular bond lengths and angles involving the non-hydrogen atoms are shown diagrammatically in Figs. 6 and 7. It should be emphasized that the bond length e.s.d.'s given are those evaluated from the

Table 8. *Magnitudes and direction cosines (D) relative to* **a**,* **b**, **c** *of the principal axes of the vibrational ellipsoids*

	i	B_i	D_1	D_2	D_3	R.M.S. displacement
S	1	2·85 Å^2	−0·936	−0·185	0·298	0·189 Å
	2	3·20	0·197	0·422	0·884	0·201
	3	2·27	−0·289	0·887	−0·358	0·169
O(1)	1	4·06	−0·752	0·059	0·655	0·226
	2	5·06	0·325	0·899	0·291	0·253
	3	2·55	0·572	−0·432	0·696	0·179
O(2)	1	4·09	−0·989	−0·138	−0·032	0·227
	2	5·49	−0·009	−0·163	0·986	0·263
	3	2·55	−0·141	0·976	0·160	0·179
N(1)	1	3·90	0·636	−0·771	−0·021	0·222
	2	4·58	0·481	0·376	0·791	0·240
	3	2·84	0·602	0·513	−0·610	0·189
N(2)	1	2·77	0·952	−0·282	−0·113	0·187
	2	5·20	0·297	0·942	0·149	0·256
	3	4·76	−0·064	0·176	−0·982	0·245
C(1)	1	2·72	−0·973	−0·007	−0·227	0·185
	2	3·15	−0·202	0·485	0·850	0·199
	3	2·39	0·104	0·874	−0·473	0·173
C(2)	1	3·14	0·224	−0·937	0·266	0·199
	2	3·40	−0·702	0·003	0·711	0·207
	3	2·64	0·676	0·346	0·650	0·182
C(3)	1	3·64	0·909	0·403	−0·099	0·214
	2	3·24	−0·332	0·562	−0·757	0·202
	3	2·72	−0·249	0·721	0·645	0·185
C(4)	1	2·73	−0·883	0·462	−0·075	0·185
	2	3·87	0·360	0·774	0·520	0·221
	3	2·59	−0·298	−0·432	0·850	0·181
C(5)	1	4·18	−0·455	0·292	0·841	0·230
	2	3·43	0·215	−0·880	0·422	0·208
	3	2·66	0·864	0·373	0·337	0·183
C(6)	1	3·23	−0·625	0·608	−0·488	0·202
	2	3·76	−0·622	−0·012	0·782	0·218
	3	2·69	0·469	0·793	0·387	0·184

Table 9. *Equation of best plane through the benzene ring in coordinate system with axes a, b, c**

$$Ax+By+Cz+D=0$$

Coefficients	Mean deviation
$A=-0·473$	0·003
$B=-0·557$	0·003
$C=\ 0·683$	0·002
$D=\ 2·247$	0·032

Individual deviations from the best plane

C(1)	−0·006 Å
C(2)	−0·002
C(3)	0·008
C(4)	−0·007
C(5)	0·000
C(6)	0·007
S	−0·046
N(2)	−0·035
H(1)	0·10
H(2)	0·05
H(3)	−0·10
H(4)	−0·10
H(7)	0·47
H(8)	0·04

least-squares matrix and that they do not take account of any additional errors due to inadequate thermal motion corrections. The mean bond lengths of the chemically equivalent bonds within the ring are given in Table 10.

Table 10. *Benzene ring mean bond lengths and (in parentheses) their standard deviations*

C(1)–C(2)	1·3931 (0·0019) Å
C(1)–C(6)	
C(2)–C(3)	1·3806 (0·0019)
C(5)–C(6)	
C(3)–C(4)	1·4015 (0·0020)
C(4)–C(5)	

The mean C–C bond length is 1·392 Å, identical with that found in crystalline benzene (Cox, Cruickshank & Smith, 1958). Although there are no significant differences between chemically equivalent pairs within the ring, the bonds parallel to the long axis of the structure and those adjacent to the amino nitrogen are significantly distorted from the standard benzene distance. The mean lengths for these bonds are 1·381 and 1·402 Å respectively. The two carbon–carbon bonds adjacent to the sulphamide group have a mean value (1·393 Å) not significantly different from those found in benzene. The distribution of bond distances within the ring of *β*-sulphanilamide bears a striking resemblance to that found in *p*-nitroaniline. The cooperative electronic interaction between the *para*-substituted amino and sulphamide groups is apparently very similar to that between the nitro and amino groups in the latter compound. As in *p*-nitroaniline, *α*-*p*-nitrophenol (Coppens & Schmidt, 1965*a*) and *β*-*p*-nitrophenol (Coppens &

Schmidt, 1965*b*) resonance forms of the quinonoid type must contribute significantly to the structure.

The C–NH_2 distance of 1·385 Å is about 0·1 Å shorter than that found in orthanilic acid (Hall, 1964) in which the nitrogen has sp^3 hybridization, but is similar to that found in structures having trigonal hybridization, *e.g.* 1·367 ± 0·003 Å in 2-amino-3-methylbenzoic acid (Brown & Marsh, 1963), 1·40 ± 0·02 Å in α-sulphanilamide (O'Connor & Maslen, 1965) and 1·371 ± 0·007 Å in *p*-nitroaniline. It is, however, significantly longer than the C–NH_2 bonds (1·316 ± 0·007 Å) in 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965).

The sulphamide group is approximately tetrahedral. The large deviation of the angle O(1)–S–O(2) (118·2°) from the ideal tetrahedral configuration probably results from the type of non-bonded interactions described by Bartell (1962). Further evidence for this conclusion is provided by examination of the non-bonded contact distances [O(1)–O(2) 2·46, O(1)–N(1) 2·43, N(1)–O(2) 2·45 Å] which indicate that the tetrahedron is distorted in a manner consistent with minimum hindrance. The double-bond character of bonds associated with the sulphamide group can be explained in terms of π-bonding molecular orbitals formed by the carbon, nitrogen and oxygen atoms with the 3*d* orbitals of the sulphur (Cruickshank, 1961). Abrahams (1956) has calculated the S–C single bond distance to be 1·82 Å, which is close to the sum of the Pauling (1960) covalent radii for sulphur and carbon. On this evidence the S–C(1) bond (1·750 Å) appears to have considerable π character. Schomaker & Stevenson (1941) have estimated the S–N single bond to be 1·74 Å, while in sulphamic acid (Sass, 1960), where the nitrogen atom has no orbitals available for π-bonding, the S–N link is 1·76 ± 0·02 Å. These are considerably greater than the S–N(1) distance in β-sulphanilamide (1·620 Å), indicating a significant degree of double-bond character for this bond. Cruickshank (1961) has assigned π-bond orders of about 0·66 for S–O bonds in the region of

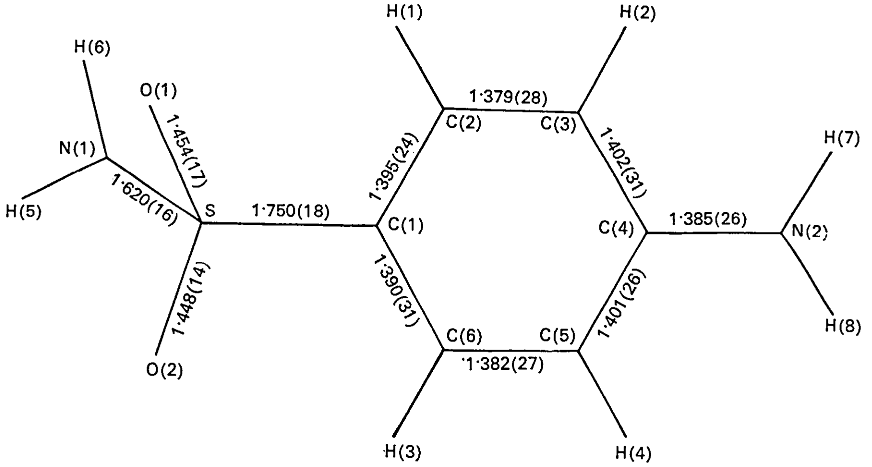

Fig. 6. Bond lengths determined from the X-ray refinement. The S–O, S–N and C–N bonds have been corrected for thermal oscillations. Standard deviations (× 10^4) are given in parentheses.

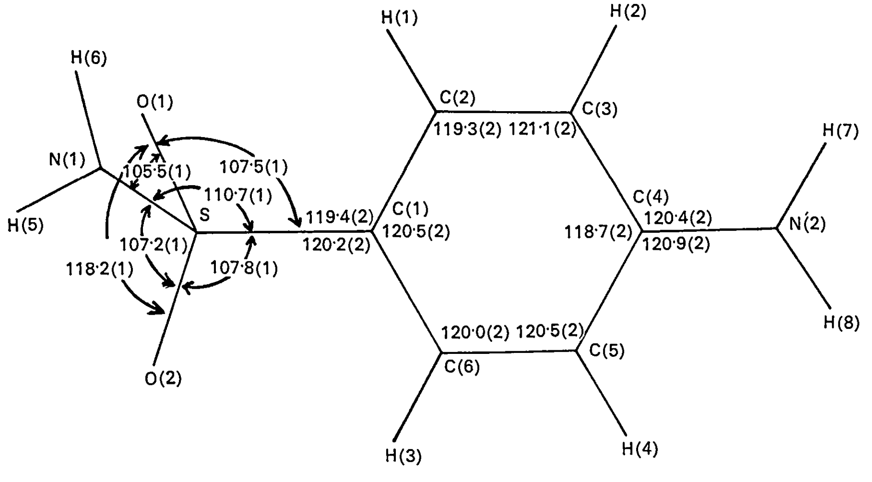

Fig. 7. Bond angles determined from the X-ray refinement. Standard deviations are given in parentheses.

1·43 Å. The two S–O bonds in β-sulphanilamide (1·454 and 1·448 Å) differ by 0·006 Å, which is significant. This may be related to the different hydrogen bond characteristics of each oxygen atom, O(1) having two intermolecular links while O(2) has only one.

Intramolecular bonds involving hydrogen

The intramolecular bonds involving hydrogen, determined from the X-ray and neutron diffraction studies, are shown in Table 11. The mean C–H distances calculated from these results are 0·99 and 1·08 Å respectively. These agree well with the recent X-ray refinement of salicylic acid (Sundaralingam & Jensen, 1965) and the neutron study of solid benzene (Bacon, Curry & Wilson, 1964). The difference observed in C–H bond lengths of the neutron and the X-ray refinements is comparable with the calculations of Stewart, Davidson & Simpson (1965), but is greater than that predicted by Cochran's (1956) theoretical study of the electron distribution in benzene. The latter author has estimated the shortening to be only 0·03 Å and concludes that even for hydrogen the spherical unbonded atom is a good model for structure refinements. More recent X-ray and neutron structure determinations have thrown considerable doubt on the validity of this conclusion, not only because of the different bond shortenings encountered but also because of the anomalously low hydrogen atom thermal parameters predicted by X-ray methods. Extension of Cochran's calculations to three dimensions (O'Connell, Rae & Maslen, 1966) still leads to an underestimation of the hydrogen atom shift. This, together with the failure of the theory to predict the central hollow in the benzene ring, may result from neglecting σ-orbital contraction effects in these calculations.

Table 11. *Bond lengths involving hydrogen atoms*

	X-ray	Neutron
H(1)–C(2)	0·93 Å	1·10 Å
H(2)–C(3)	0·98	1·10
H(3)–C(5)	0·99	1·03
H(4)–C(6)	1·03	1·07
H(5)–N(1)	0·88	1·00
H(6)–N(1)	0·89	1·00
H(7)–N(2)	1·11	1·04
H(8)–N(2)	0·88	0·97

The mean standard deviation in these bonds is 0·035 Å.

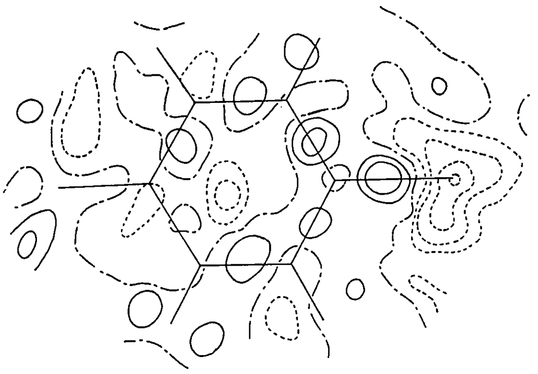

Fig. 8. Final difference synthesis calculated in the molecular plane. Zero contour chain dotted, negative contours dashed, positive contours full lines; at intervals of 0·1 e.Å^{-3}.

Three of the four amino hydrogen atoms are involved in intermolecular bonds and the mean N–H bond lengths for these are 0·88 and 0·99 Å for the X-ray and neutron diffraction results respectively, the differences being similar to those generally reported. The results for the N(2)–H(7) bond, however, are anomalous, since the X-ray bond length is 0·07 Å larger than the neutron value. The latter is not expected to be particularly reliable because of the overlap of H(7) with the amino nitrogen in the [010] projection, but it is more likely that it is the X-ray result which is in error, for this is more than 0·2 Å greater than those for the other three N–H bonds. H(7) is the only amino hydrogen atom not involved in hydrogen bonding, and its extraordinarily high B value in the X-ray analysis suggests that it has a high degree of freedom, which may have affected the accuracy of the determination of the X-ray parameters. Nevertheless it is not clear why this effect should not have been observed in the neutron structure analysis.

Electron density distribution

A section of the final difference synthesis, calculated in the molecular plane, is shown in Fig. 8. The distribution of this difference density may be explained in terms of atomic antisymmetry effects resulting from electron redistribution at bonding (Dawson, 1965). Trigonally bonded carbon may be represented by the superposition of a symmetric component of the electron density which is largely eliminated in the difference synthesis and an antisymmetric component which remains. This component contains a positive peak of density along each of the bonds with a corresponding antisymmetric negative peak related through the atomic position. In practice, for an aromatic ring the smearing effects associated with thermal motion give rise to overlap of the hollows within the ring, resulting in a continuous central negative region. The positive features between the carbon and hydrogen atoms are also missing from X-ray difference syntheses owing to a radial shift of the hydrogen atom from the nucleus to a position closer to the ring.

The carbon–sulphur and all carbon–carbon bonds contain areas of residual electron density about half way between the atomic sites. Although only the peaks in the bond C(1)–C(6) and C(1)–S are significant when compared with the e.s.d. in the electron density, the consistency from bond to bond indicates that this is a real effect resulting from the aspherical nature of the electron density in the bonded atom. There is a negative area near the ring centre resulting from the overlap of adjacent antisymmetric peaks with a minimum density of $-0·27$ e.Å^{-3}.

Sections through the eight planar bonds of the molecule taken perpendicular to the benzene ring are shown in Fig. 9. The residual bond peaks have a mean extension of approximately 0·5 Å above and below the molecular plane. These results are consistent with the difference density distribution observed in the structure of orthanilic acid (Hall, 1964). It has been suggested (Rabinovich & Hirshfeld, 1964) that extensions of this type result from concentrations of π-electrons at the bond centre. Recent studies of the residual density in C–C bonds (O'Connell, Rae & Maslen, 1966) have shown, however, that similar distributions can occur in single bonds and that the residual density shape is probably largely dependent on bond environment and the interaction of the anti-symmetric regions of electron density (Dawson, 1965). Theoretical calculations of the difference density in benzene (O'Connell, Rae & Maslen, 1966) have indicated that the extension of the bond peak results from the interaction of the dumbell π-electron orbitals with the axially symmetric σ-electron density. It must be emphasized that the residual density observed by the X-ray method is the difference between the true distribution and the spherically symmetric model postulated and should not be interpreted as representing the actual valence electron distribution.

The sulphur atom appears in a region of negative electron density with a minimum at the atomic site of 0·4 e.Å^{-3}, which is highly significant. It is unlikely that this results from systematic errors in the data since considerable care was taken in the intensity measurements and scaling procedures. Furthermore, a similar electron distribution near the sulphur atom has been noted in the final difference synthesis of orthanilic acid. A more probable explanation is that the discrepancy arises from errors in the isolated atom scattering curve for sulphur, which must differ considerably from the bonded-atom form factor.

The distribution of residual density about a tetrahedrally bonded system may be explained in a manner analogous to the trigonal case described above. The antisymmetric component consists of a positive peak between each pair of bonded atoms with a related region of negative density along the extension of the bond (Dawson, 1965). In practice the positive density regions will probably only exist for non-terminal atoms since the least-squares refinement will predict positions closer to the central atom in the terminal case, thus eliminating the bond peak. The sulphamide group is of particular interest because it provides evidence of the residual electron distribution about a tetrahedral configuration containing both terminal and non-terminal atoms. Fig. 10 shows the six sections of the difference synthesis drawn through the sulphur and the other pairs of atoms of this group. The difference density is exactly as expected for a system of one non-terminal and three terminal atoms. Only the carbon–sulphur bond has a region of residual charge between the atoms. The nitrogen and the two oxygen atoms are shifted towards the sulphur and lie close to zero contours. The anti-symmetric electron deficient region evident on the extension of each bond is in accord with Dawson's theoretical predictions.

The asymmetric nature of the residual density about the amino nitrogen in the molecular plane may result from the asphericity of this atom caused by the localization of the lone pair hybrid. The difference density is similar to that predicted by Dawson (1964) and the angles that the bond N(2)–C(4) makes with the benzene ring differ by 0·5° in the expected direction.

Packing

The hydrogen bond network proposed by Alléaume & Decap (1965*b*) has been confirmed by the positive identification of the hydrogen atoms from the neutron diffraction analysis. The intermolecular distances and the angles subtended at the hydrogen atoms are given in Table 12. The N(2)–H(8)···O(1) bond is linear and apparently provides the strongest intermolecular cohesive force. The remaining two bonds are distorted by 27° from the N···O direction, and the N(1)–H(5)···

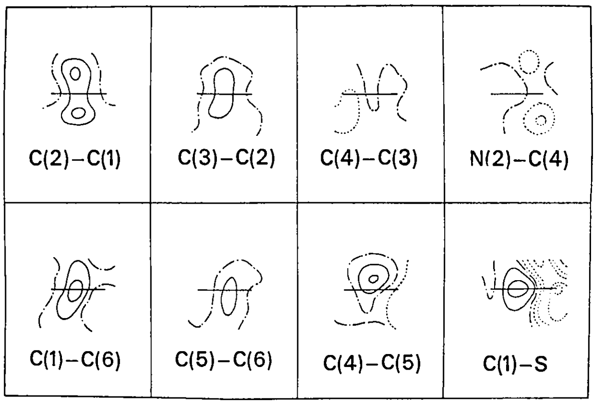

Fig. 9. Difference syntheses perpendicular to the benzene ring and through the eight planar bonds. Zero contour chain dotted, negative contours dashed, positive contours full lines; at intervals of 0·1 e.Å^{-3}.

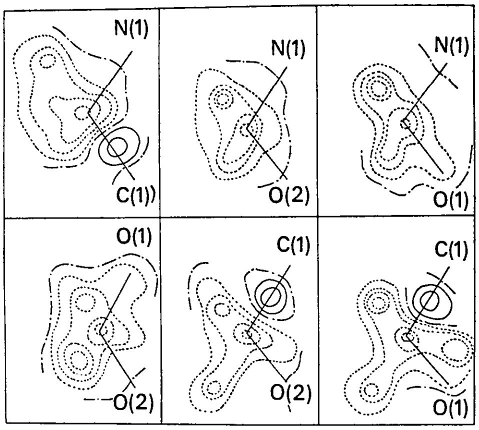

Fig. 10. Difference syntheses in the sulphamide group, drawn through the sulphur atom. Zero contour chain dotted, negative contours dashed, positive contours full lines; at intervals of 0·1 e.Å^{-3}.

O(1) link is 0·09 Å shorter than the N(1)–H(6)···O(2) bond. The hydrogen bond system is similar to that found in sulphamide (Trueblood & Mayer, 1956) and α-sulphanilamide (O'Connor & Maslen, 1965). In the latter structure the packing forces are provided by three N–H···O bonds similar to those in β-sulphanilamide. It is interesting to note, however, that the density of the β crystals (1·514 g.cm^{-3}) is significantly greater than that of the α form (1·479 g.cm^{-3}), indicating that the molecules are much more closely packed and that van der Waals interactions play a more important role in the intermolecular packing. A comparison with the structures of metanilic acid (Hall & Maslen, 1965), sulphanilic acid monohydrate (Rae & Maslen, 1962) and orthanilic acid (Hall, 1964), all of which have the zwitterion configuration, shows the N–H···O bonds between charged atoms to be about 0·25 Å shorter than those found in β-sulphanilamide.

Table 12. *Hydrogen bond contact distances and angles*

	Angle at H	N–O distance
$N(1)_{II}$–$H(5)\cdots O(1)_{IV}$	152·5°	3·028 Å
$N(2)_{I}$–$H(8)\cdots O(1)_{IV}$	180·0	3·055
$N(1)_{II}$–$H(6)\cdots O(2)_{III}$	153·5	3·118

I, II, III and IV refer to the equivalent positions x, y, z; $1+x,y,z$; $1-x,\frac{1}{2}+y,\frac{1}{2}-z$; and $1+x,\frac{3}{2}-y,\frac{1}{2}+z$ respectively.

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References

Abrahams, S. C. (1955). *Acta Cryst.* **8**, 661.

Alléaume, M. & Decap, J. (1965*a*). Private communication.

Alléaume, M. & Decap, J. (1965*b*). *Acta Cryst.* **18**, 731.

Bacon, G. E. (1962). *Neutron Diffraction.* Oxford: Clarendon Press.

Bacon, G. E., Curry, N. A. & Wilson, S. A. (1964). *Proc. Roy. Soc.* A, **279**, 98.

Bartell, L. S. (1962). *Tetrahedron,* **17**, 177.

Brown, G. M. & Marsh, R. E. (1963). *Acta Cryst.* **16**, 191.

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180.

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Cady, H. & Larson, A. C. (1965). *Acta Cryst.* **18**, 485.

Cochran, W. (1956). *Acta Cryst.* **9**, 924.

Coppens, P. & Schmidt, G. M. T. (1965*a*). *Acta Cryst.* **18**, 62.

Coppens, P. & Schmidt, G. M. T. (1965*b*). *Acta Cryst.* **18**, 654.

Cox, E. G., Cruickshank, D. W. J. & Smith, J. A. S. (1958). *Proc. Roy. Soc.* A, **247**, 1.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1961). *J. Chem. Soc.* p. 5486.

Dawson, B. (1964). *Acta Cryst.* **17**, 990.

Dawson, B. (1965). *Aust. J. Chem.* **18**, 595.

Grenville-Wells, H. J. (1955). *Acta Cryst.* **8**, 512.

Hall, S. R. (1964). Ph.D. Thesis, Univ. of Western Australia.

Hall, S. R. & Maslen, E. N. (1965). *Acta Cryst.* **18**, 301.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

Ibers, J. A. (1956). *Acta Cryst.* **9**, 652.

James, R. W. (1948). *The Crystalline State.* Vol. II. London: Bell.

Jensen, L. H. & Sundaralingam, M. (1964). *Science,* **145**, 1185.

Mair, G. A. (1962). Private communication.

McLachlan, D. (1957). *X-ray Crystal Structure.* New York: McGraw-Hill.

O'Connell, A. M., Rae, A. I. M. & Maslen, E. N. (1966). *Acta Cryst.* **21**, 208.

O'Connor, B. H. & Maslen, E. N. (1965). *Acta Cryst.* **18**, 363.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Rabinovich, D. & Hirshfeld, F. L. (1964). *Israel J. Chem.* **2**, 82.

Rae, A. I. M. & Maslen, E. N. (1962). *Acta Cryst.* **15**, 1285.

Rietveld, H. M. (1963). Ph.D. Thesis, Univ. of Western Australia.

Rollett, J. S. & Sparks, R. A. (1960). *Acta Cryst.* **13**, 273.

Sass, R. L. (1960). *Acta Cryst.* **13**, 320.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). A.C.A. Winter Meeting.

Sundaralingam, M. & Jensen, L. H. (1965). *Acta Cryst.* **18**, 1053.

Trueblood, K. N. & Mayer, S. W. (1956). *Acta Cryst.* **9**, 628.

Trueblood, K. N., Goldish, E. & Donohue, J. (1961). *Acta Cryst.* **14**, 1009.

Vand, D. & Dunning, A. J. (1965). A.C.A. and M.S.A. June Meeting.

Watanabe, A. (1941). *Naturwissenschaften,* **29**, 116.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151.

Yakowitz, M. L. (1948). *J. Ass. Off. Agric. Chemists, U.S.A.* **31**, 656.