neighboring chains is 3·495 ($\sigma=0{\cdot}003$) Å. This is considerably closer than the 4·40 Å predicted on the basis of van der Waals interactions alone (Von Hippel, 1948). The same 'contraction' was observed in trigonal selenium (Cherin & Unger, 1966). However, this effect is more pronounced in tellurium.

The authors would like to acknowledge the help of R. Keezer, who supplied the single tellurium crystals.

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The crystal structure of 2,2′-diaminodiphenyl disulphide.

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2,2′-Diaminodiphenyl disulphide crystallizes in space group *Pbca* with $a=8{\cdot}211$, $b=13{\cdot}144$, $c=22{\cdot}766$ Å and $Z=8$. The crystal structure was solved and the molecular conformation determined without emphasis on high accuracy. The dihedral angle across the S–S bond is 87°, those across the S–C bonds are 86 and 85° respectively. There is suggestive evidence that hydrogen bonds between the amino groups tie the molecules to chains roughly parallel to the *b* axis.

During the course of investigations on thioaromatic compounds, carried out in this laboratory, interest arose in the molecular conformation of 2,2′-diaminodiphenyl disulphide, $H_2N\text{–}C_6H_4\text{–}S\text{–}S\text{–}C_6H_4\text{–}NH_2$.

Experimental

The substance was obtained in the form of thin, yellow platelets, whose X-ray powder diagram was indexed on the basis of a hexagonal unit cell: $a=13{\cdot}144\pm0{\cdot}005$, $c=8{\cdot}211\pm0{\cdot}004$ Å (λ Cu $K\alpha_1=1{\cdot}54050$ Å).

Single-crystal X-ray diffraction data revealed that the structure is in fact orthorhombic: $a=8{\cdot}211$, $b=13{\cdot}144$, $c=22{\cdot}766$ Å; $c/b=\sqrt{3}$. The space group, *Pbca*, is uniquely determined by systematic absences. The general position is eightfold; with $Z=8$ the calculated density is $d_x=1{\cdot}34$ g.cm^{-3}, a normal value for this sort of compound.

Three-dimensional intensity data were collected by means of the PAILRED automatic diffractometer, using crystal-monochromatized Cu $K\beta$ radiation. The integrated intensities of 369 reflexions having $\sin\theta/\lambda\le0{\cdot}36$ Å^{-1} were measured and corrected for Lorentz and polarization effects, but not for absorption.

Structure determination

The positions of the sulphur atoms were derived directly from the sharpened Patterson map. Approximate coordinates of all carbon and nitrogen atoms were found by the use of combined Fourier and vector-search methods. In the ensuing full-matrix, least-squares refinement the quantity $\Sigma w(|F_o|-|F_c|)^2$ was minimized with respect to the coordinates of the above atoms, as well as their individual, isotropic *B* parameters. Only first derivatives of the structure factors were considered. Hydrogen atoms were excluded. The weighting scheme was based on counting statistics, a lower limit of 2% being set for the relative error in the measurement of strong reflexion intensities. The atomic scattering factors employed were from *International Tables of X-ray Crystallography* (1962).

The refinement yielded a final *R* index of 16·7% and a final *weighted R* index of 5·7%, defined as

$$R=\frac{\Sigma\,||F_o|-|F_c||}{\Sigma\,|F_o|}\ \text{and}\ R_w=\frac{F_c||\Sigma w||F_o|-|}{\Sigma w|F_o|}$$

respectively. The average coordinate shift in the last refinement cycle was about 0·04 times the estimated standard deviation; the largest relative shift was almost four times as large. The standard deviations were estimated from the least-squares residuals. They are given together with the atomic parameters in Table 1. Since absorption corrections were not applied, the *B* values quoted there have no direct physical meaning. Table 2 contains a list of observed and calculated structure factors.

Discussion

No attempts have been made in the present study to attain a high degree of accuracy, because this is not required for the determination of the molecular conformation. *A priori*, therefore, appreciable standard deviations of the coordinates were expected, but the magnitude of the estimated standard deviations (up to 0·6 Å) associated with the coordinates of C(*B*3), C(*B*5) and C(*B*6) exceeds all expectations and remains unexplained. Yet there are no indications that these atoms are wrongly sited, neither from the calculated values of R_w and of the *B* parameters, nor from the 3-D electron-density synthesis. Moreover, the positions of these atoms are within about 0·1 Å of those computed with the use of the most reliably determined structure parameters and assuming ring *B* to be a regular hexagon with sides of 1·39 Å.

In order to diminish the effect of the above inaccuracies the centres of gravity of the aromatic rings, *G*(*A*) and *G*(*B*), which can be located with greater precision than the individual carbon atoms, were taken as points of reference for subsequent calculations of bond distances and angles.

Table 1. *Atomic parameters and their standard deviations* ($\times 10^3$)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
S(*A*)	0·321	1	0·5132	0·6	0·1644	0·3	5 Å^2
S(*B*)	0·528	1	0·5611	0·6	0·2073	0·4	5
N(*A*)	0·145	2	0·715	1	0·179	1	3
N(*B*)	0·653	2	0·347	1	0·230	1	4
C(*A*1)	0·308	3	0·602	2	0·100	1	1
C(*A*2)	0·198	3	0·693	2	0·120	2	2
C(*A*3)	0·174	3	0·761	2	0·067	1	3
C(*A*4)	0·232	3	0·738	3	0·018	2	4
C(*A*5)	0·321	3	0·655	2	0·001	1	6
C(*A*6)	0·359	4	0·576	2	0·044	2	5
C(*B*1)	0·698	4	0·496	2	0·166	2	3
C(*B*2)	0·740	6	0·392	2	0·186	3	2
C(*B*3)	0·876	26	0·353	46	0·150	14	4
C(*B*4)	0·942	8	0·417	9	0·108	2	5
C(*B*5)	0·911	21	0·513	17	0·089	10	5
C(*B*6)	0·763	23	0·558	14	0·123	6	3

Table 2. *Observed and calculated structure factors*

Within each group the columns, reading from left to right, contain the values of *l*, $10F_o$ and $10F_c$.

0 0 l		
16	-40	-39
14	-41	-33
12	37	61
10	114	116
8	-79	-78
6	219	224
4	-201	-207
2	-180	-189
0 2 l		
16	-60	-109
15	16	9
14	-19	-28
13	52	30
12	18	9
11	-115	-116
10	23	4
9	45	51
8	-99	-106
7	-35	-23
6	79	77
5	-12	-25
4	-193	-192
3	-108	-104
2	-230	-230
1	-69	-75
0	283	291
0 4 l		
14	-24	-5
13	84	87
12	113	114
11	-40	-16
10	-63	-73
9	60	22
8	-126	-125
7	-13	-22
6	138	133
5	-88	-92
4	-102	-101
3	63	62
2	24	3
1	-202	-196
0	141	142
0 6 l		
12	116	137
11	-29	-46
10	-88	-118
9	19	11
8	53	51
7	-83	-88
6	120	123
5	87	90
4	-59	-56
3	55	50
2	-72	-80
1	-247	-260
0	-15	-13
0 8 l		
8	-17	-48
7	-42	-16
6	79	71
5	39	34
4	-49	-34
3	-20	-18
2	47	32
1	19	13
0	21	33
1 0 l		
16	26	32
14	-66	-48
12	-38	-51
10	63	83
8	-135	-148
6	-14	-27
4	-140	-142
2	-105	-111
1 1 l		
16	-18	-24
15	51	10
14	21	12
13	17	5
12	-13	-6
11	-18	-37
10	-38	-36
9	-15	-9
8	16	8
7	-100	-96
6	18	11
5	284	296
4	11	18
3	-120	-125
2	-27	-30
1	53	52
1 2 l		
15	27	55
14	-27	-61
13	-16	-7
12	76	72
11	-19	-45
10	39	40
9	-22	-18
8	-73	-77
7	-37	-31
6	15	0
5	-100	-89
4	78	90
3	105	97
2	134	126
1	-239	-238
1 3 l		
15	-15	-3
14	24	35
13	-18	-17
12	-43	-33
11	-13	-8
10	-15	-21
9	-92	-92
8	63	66
7	44	59
6	-104	-112
5	113	103
4	96	83
3	-193	-194
2	-232	-228
1	28	33
1 4 l		
14	-57	-38
13	-16	-8
12	19	22
11	-15	-33
10	60	48
9	97	117
8	-106	-105
7	49	51
6	-83	-84
5	24	26
4	147	150
3	-57	-51
2	-146	-145
1	44	50
1 5 l		
13	20	39
12	-18	-6
11	-19	-5
10	-51	-68
9	-45	-41
8	86	85
7	66	76
6	-129	-112
5	-33	-14
4	108	99
3	-12	-12
2	-36	-40
1	-15	-26
1 6 l		
12	-41	-21
11	-15	-6
10	23	15
9	57	67
8	-51	-31
7	-47	-57
6	52	66
5	-18	-34
4	119	114
3	25	14
2	-12	-2
1	18	14
1 7 l		
10	16	19
9	-45	-28
8	-15	-20
7	90	85
6	-60	-52
5	-15	-20
4	53	57
3	-23	-12
2	-12	-5
1	-18	-4
1 8 l		
8	-14	-4
7	-17	-28
6	16	0
5	-31	-38
4	-18	-8
3	38	5
2	-39	-27
1	24	18
1 9 l		
4	28	37
3	19	13
2	17	12
1	-19	-10
2 0 l		
14	77	89
12	-124	-132
10	86	80
8	-62	-58
6	-190	-187
4	134	134
2	-101	-107
2 1 l		
14	21	4
13	-55	-70
12	-25	-3
11	62	65
10	-11	-6
9	-41	-22
8	-61	-68
7	-11	-20
6	62	54
5	80	76
4	-145	-140
3	-236	-230
2	-37	-31
1	-80	-80
0	94	87
2 2 l		
14	62	66
13	42	52
12	-84	-87
11	-21	-3
10	118	129
9	103	87
8	12	12
7	-126	-118
6	-111	-111
5	-59	-64
4	158	150
3	230	218
2	56	58
1	-31	-59
0	100	91
2 3 l		
14	24	42
13	-40	-57
12	-37	-48
11	17	29
10	46	29
9	41	9
8	42	52
7	-12	-10
6	-19	-5
5	15	14
4	9	16
3	11	8
2	-67	-73
1	-150	-137
0	-190	-179
2 4 l		
13	43	52
12	-65	-45
11	-88	-71
10	73	77
9	73	69
8	45	13
7	-69	-74
6	-90	-99
5	-41	-26
4	43	48
3	120	121
2	-17	-8
1	-80	-75
0	-92	-84
2 5 l		
12	-13	-6
11	42	62
10	53	76
9	18	17
8	-16	0
7	-43	-31
6	-48	-54
5	16	12
4	99	112
3	16	38
2	-13	-27
1	14	13
0	30	57
2 6 l		
10	22	7
9	57	59
8	27	10
7	20	17
6	-82	-67
5	-72	-71
4	14	4
3	51	39
2	105	113
1	16	18
0	-80	-75
2 7 l		
8	16	18
7	-67	-61
6	-40	-19
5	105	105
4	-44	-10
3	16	8
2	-17	-4
1	-65	-69
0	-45	-48
2 8 l		
5	-44	-31
4	-30	-43
3	-28	-21
2	63	65
1	-25	-2
0	-119	-123
3 0 l		
12	22	1
10	62	59
8	-71	-86
6	-14	-8
4	20	47
2	106	102
3 1 l		
13	-56	-69
12	-18	-1
11	-41	-53
10	-19	-12
9	133	118
8	79	66
7	-98	-105
6	-62	-77
5	12	12
4	49	58
3	45	36
2	-95	-98
1	-132	-125
3 2 l		
13	-44	-19
12	43	6
11	69	57
10	-26	-59
9	23	14
8	-65	-79
7	-29	-54
6	15	29
5	63	77
4	-39	-37
3	-18	-17
2	13	14
1	-18	-3
3 3 l		
12	16	7
11	-36	-32
10	-61	-72
9	188	176
8	102	92
7	-132	-139
6	-42	-43
5	15	11
4	105	108
3	183	177
2	64	80
1	-34	-53
3 4 l		
12	20	31
11	32	32
10	-43	-16
9	-21	-35
8	19	6
7	-65	-74
6	48	54
5	97	101
4	16	20
3	-56	-65
2	14	7
1	-26	-29
3 5 l		
10	16	7
9	76	82
8	52	46
7	-26	-27
6	-23	-37
5	-88	-90
4	18	20
3	83	69
2	-66	-56
1	29	14
3 6 l		
9	28	16
8	34	22
7	-20	-7
6	-21	-23
5	25	15
4	-23	-9
3	17	1
2	19	26
1	16	7
3 7 l		
6	23	8
5	-125	-127
4	-28	-3
3	135	132
2	-14	-3
1	-61	-52
4 0 l		
12	-96	-85
10	94	110
8	32	19
6	26	13
4	33	19
2	-21	-31

The S–S bond distance is 2·1 Å, S–C(1) 1·8 Å, the angle S–S–*G* is 106° at S(*A*) and 104° at S(*B*). This is in close agreement with the corresponding *p,p'*-dibromo compound (Toussaint, 1945).

Some dihedral angles of interest (the planes involved are indicated between square brackets) are

[*G*(*A*)–S(*A*)–S(*B*)] ∧ [S(*A*)–S(*B*)–*G*(*B*)]	87°
[*G*(*A*)–S(*A*)–S(*B*)] ∧ [Ring *A*]	86
[S(*A*)–S(*B*)–*G*(*B*)] ∧ [Ring *B*]	85
[Ring *A*] ∧ [Ring *B*]	29

The N(*A*)–· · ·N(*B'*) distance of 3·2 Å is indicative of a hydrogen bond (Pauling, 1960), which ties the molecules to chains roughly parallel to the *b* axis (Fig. 1).

Further work on this compound is not contemplated.

Dr J. Van der Veen supplied the problem as well as the crystals. Miss C. Kortleve and Mr J. I. Leenhouts were responsible for the automatic computations. Their contributions are gratefully acknowledged.

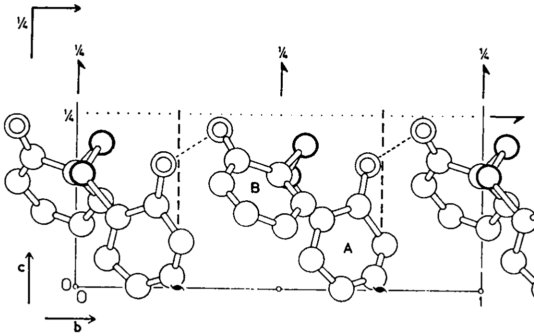

Fig. 1. Projection of the structure along the *a* axis. Hydrogen bond represented by broken line.

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