L'écart de chaque atome a ce plan est respectivement:

C(1)	−0,14 Å	C(7)	0,05 Å	O(1)	−0,96 Å
C(2)	−0,19	C(8)	0,09	O(2)	0,77
C(3)	0,13	C(9)	0,01	O(3)	−0,19
C(4)	0,06	C(10)	0,04	O(4)	−0,56
C(5)	0,11	C(11)	−0,26		
C(6)	0,11				

On remarque que ces atomes se répartissent de façon que les carbones directement liés au groupement carboxylique s'éloignent le plus du plan moyen de la chaine.

Les liaisons hydrogènes assurant la polymérisation des molécules sont à peu près semblables à chaque extrémité c'est ainsi que l'on trouve:

Pour le groupement initial: O(2)· · ·O(1′) = 2,687 Å
Pour le groupement terminal: O(4)· · ·O(3′) = 2,668

L'étude de cette série va se poursuivre jusqu'à l'acide en C(13); nous indiquerons à la suite de la description de cette structure les caractéristiques structurales de cette série.

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The Crystal and Molecular Structure of Sulfur Dicyanide

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(*Received* 10 *January* 1966 *and in revised form* 11 *April* 1966)

The crystal structure of sulfur dicyanide, $S(CN)_2$, has been determined. The crystal is orthorhombic, space group *Pbca*, a = 8·56, b = 6·87, c = 12·84 Å. The molecules are planar with C_{2v} symmetry. The average C–N distance is 1·12 Å, and the average S–C distance is 1·73 Å. Both nitrogen atoms are involved in weak interactions with neighboring sulfur atoms. The coordination at the sulfur atom is roughly square planar.

Introduction

The structures of quite a number of molecular cyanides have been determined by X-ray diffraction in recent years. These have all exhibited one feature in common: a nitrogen-to-heavy-atom distance 0·4–0·5 Å shorter than one would predict from Pauling's van der Waals radii (Pauling, 1960). In addition, the determinations of simple Group V cyanide structures (Emerson & Britton, 1963, 1964) have shown that in these compounds the bond angle at the cyanide carbon is significantly smaller than 180°. This deviation from linearity does not occur in the Group VII cyanides (Heiart & Carpenter, 1956). The structure of $Se(CN)_2$ has been reported by Hazell (1964), but the determination was done only in projections and the bond distances and angles obtained are admittedly unreliable. Hazell also reported that $S(CN)_2$ is isomorphous with $Se(CN)_2$. At the time this note appeared, the present author had collected preliminary data on $S(CN)_2$; these indicated that the space group was different from that reported by Hazell for $Se(CN)_2$. It therefore seemed of some interest to proceed with the complete structure determination, both to resolve this conflict over the space group and to obtain more reliable bond distances and angles for a simple Group VI cyanide.

Experimental

$S(CN)_2$ was prepared as described by Söderback (1919) and purified by vacuum sublimation. The tabular white crystals are not especially hygroscopic, and can be handled for short periods in air, but they decompose slowly even in tightly sealed bottles to give a brownish, flaky material. Crystals suitable for X-ray diffraction work were sealed inside thin-walled borosilicate glass capillaries. Two sets of data were obtained. From one crystal, Weissenberg photographs of levels 0–5 about [011] as a rotation axis were obtained with Cu $K\alpha$ radiation. Photographs of the sixth layer were also collected, but these data correlated so poorly with the other layers that they were excluded from the refinement. From a second crystal, precession photographs of levels 0*kl*–4*kl* were collected with Mo $K\alpha$ radiation. Of the approximately 700 independent reflections within the sphere of reflection for Cu $K\alpha$ radiation, 291 were observed. Intensities were estimated visually by comparison with a standard intensity strip prepared from one of the crystals by timed exposures. Lorentz and polarization corrections were applied in the usual manner, using programs written for this purpose at Montana State University. Both crystals were very small – 0·2 to 0·3 mm in the largest dimension – and absorption corrections were judged to be negligible.

Space group and unit cell

The following extinctions were observed: h odd when $l=0$, k odd when $h=0$, l odd when $k=0$. There are therefore three mutually perpendicular glide planes and the space group is uniquely determined as $Pbca$ (D_{2h}^{15}). The unit cell dimensions were determined by careful measurements on Weissenberg and rotation photographs of the crystals. The camera diameter was determined by measuring it several times with a precision micrometer and averaging the results. Allowance was made for film thickness in the calculation. The following cell dimensions were obtained:

$$a = 8{\cdot}56 \pm 0{\cdot}01 \text{ Å}$$
$$b = 6{\cdot}87 \pm 0{\cdot}01$$
$$c = 12{\cdot}84 \pm 0{\cdot}01$$

If one assumes that $Z=8$, the density of $S(CN)_2$ calculated from these dimensions is 1·48 g.cm^{-3}. Prestegard (1963) has estimated that the density is 1·4 g.cm^{-3} as a lower limit, in good agreement.

Determination of structure

A three-dimensional Patterson map was calculated. The S–S interactions were readily apparent, and the position of the sulfur atom was easily deduced. None of the lighter atoms were particularly obvious in the Patterson map. Structure factors were calculated using the approximate sulfur position and an electron density map, using observed amplitudes and signs determined by the sulfur atoms, was computed. The positions of the two cyanide groups were quite apparent in this map. Least-squares refinement was begun immediately with a program written by J. A. Mair and kindly sent to me by Professor Bruce Penfold. The program minimizes the function $E=\Sigma\, w[(kF_o)^2-(F_c)^2]^2$, and uses a block diagonal approximation for calculating parameter shifts. Only observed reflections were included in the refinement. The weighting scheme used assigned the weights as follows:

$$\sqrt{w} = \frac{1}{\left\{1+\left(\frac{kF_o-b}{a}\right)^2\right\}^{\frac{1}{2}}}$$

where a and b are assigned at the beginning of each cycle of refinement. At the beginning of the refinement, a was set equal to 50 and b to 30. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

The structure refined in nine cycles from an R index* of 0·39 to 0·17. Refinement at this stage was proceeding very slowly, and the two C–N bond lengths differed by 0·1 Å. A careful examination of the data suggested that there might be systematic scaling errors. The original scaling had been done in the following way: the five layers of precession data were scaled to each other using a single [011] zone precession films, and the scale factors for each Weissenberg layer relative to this block of precession data were then determined. The scaling, therefore, rested heavily on the [011] zone photograph which had only a relatively small number of reflections visible on some row lines. Because of the geometry of the collecting process, the common practice of refining scale factors for the individual Weissenberg layers was impractical. Instead, the data were rescaled with the use of following scheme:

1. All ratios P_i/W_j for reflections common to both blocks of data were determined, where P_i is an unscaled precession datum from the ith layer and W_j is an unscaled Weissenberg datum from the jth layer.
2. Average values of $\overline{P_i/W_j}$ for fixed i and j were calculated.
3. By dividing $\overline{P_i/W_j}$ by $\overline{P_i/W_k}$, ratios $\overline{W_k/W_j}$ could be determined. Average values of $\overline{W_k/W_j}$ were calculated, weighting the various ratios according to the number of observations involved. Average values of $\overline{P_i/P_j}$ were calculated in the same way.
4. $\overline{P}_4$ was set equal to 1·0 and all other scale factors calculated relative to this arbitrary point. The set of scale factors so obtained differed significantly from the original set.

Refinement was resumed with these rescaled data. The C–N bond lengths improved immediately, and in six more cycles R was reduced to 0·14. Then a was set equal to 10 and b to 12 in the weighting factor expression. Three more cycles of refinement reduced R to 0·12. The positions of all the atoms at this point in the refinement were within one standard deviation of the final values obtained after complete anisotropic refinement.

At this stage, an anisotropic temperature factor was assigned to the sulfur atom and refinement was continued for five more cycles. Anisotropic temperature factors were then assigned to all atoms and nine more cycles of refinement carried out. These reduced R to 0·106 and all shifts to less than ten per cent of the standard deviations.

As an experiment, the weighting scheme was altered again at this point. The parameter a was set equal to 1·0 and b to zero. After six cycles of refinement it was clear that the process was diverging. When a was raised to ten again, with b still zero, the refinement converged in six more cycles to an R value of 0·106, with the position parameters essentially unchanged.

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* The program calculates the agreement index $R=\Sigma\,|(kF_o-F_c)|/\Sigma\, kF_o$ at the end of each cycle.

Table 1. *Observed and calculated structure factors*

l	100F_o	100F_c
0, 0, *l*		
2	151*	475
4	6833	-10607
6	691	-673
8	4032	4155
10	502	439
12	1419	-1593
14	377*	-219
16	314	535
0, 2, *l*		
1	1080	-986
2	1030	936
3	1143	-1305
4	2386	2424
5	653	748
6	1331	-1276
7	1269	1139
8	1495	-1420
9	678	-644
10	678	669
11	728	-704
12	691	714
13	502	445
14	364*	-305
0, 4, *l*		
0	1055	-1035
1	754	571
	276*	-118
3	1030	903
4	1055	1035
5	502	-509
6	427*	369
7	1017	-1033
8	867	-830
9	590	462
10	490*	-514
11	779	782
12	427*	441
0, 6, *l*		
0	1645	1740
1	377*	-37
2	352*	141
3	414*	-337
4	1457	-1409
0, 8, *l*		
1	502	-816
2	440	75
1, 0, *l*		
2	553	-577
4	1696	2261
6	427	359
8	1369	-1628
10	389*	-206
12	804	814
1, 1, *l*		
1	352	382
2	4157	-5375
3	942	-995
4	502	-446
5	264*	-178
1, 1, *l*		
6	2788	3118
7	1005	932
8	440	419
9	440	277
10	1507	-1595
11	590	-562
12	427*	-273
13	414*	-215
14	653	694
15	301*	272
1, 2, *l*		
1	942	835
2	3894	3647
3	1231	-1084
4	226*	-109
5	264*	-118
6	1557	-1524
7	628	595
8	352*	195
1, 3, *l*		
1	3090	-2847
2	226*	-169
3	2587	2358
4	314*	-190
5	2072	2113
6	364*	134
7	1331	-1381
8	414*	279
9	1181	-1220
10	440*	-87
11	703	720
12	414*	-275
13	628	616
14	314*	40
1, 4, *l*		
1	427	-448
2	490	-472
3	854	744
4	239*	296
4	239*	296
5	352*	15
6	603	474
7	628	-542
8	389*	-224
1, 5, *l*		
1	867	918
2	1959	1971
3	791	-841
4	289*	398
5	829	-801
6	1821	-1433
7	590	546
8	590	-506
9	628	600
10	779	789
11	389*	-223
1, 6, *l*		
1	578	536
2	352*	182
3	528	-446
4	327*	134
5	666	-380
6	465*	-102
1, 7, *l*		
1	389*	485
2	377*	-490
1, 7, *l*		
4	352*	-9
2, 0, *l*		
0	2010	1768
2	565	515
4	1746	-1829
6	829	-836
8	1633	1582
10	678	657
12	1206	-957
2, 1, *l*		
0	929	904
1	2135	-1872
2	138*	211
3	2010	-2132
4	553	-569
5	477	405
6	477	-421
7	1206	1004
8	339*	169
2, 2, *l*		
0	1218	-1022
1	3102	-3033
2	653	-575
3	2487	-2369
4	804	853
5	2085	2199
6	929	863
7	1181	1335
8	565	-560
9	1156	-1165
10	603	-578
11	829	-733
12	414*	290
13	603	531
14	427	262
15	301*	347
2, 3, *l*		
0	929	901
1	226*	34
2	226*	-39
3	264*	-247
4	791	-770
5	327*	-242
6	339*	70
7	377*	169
8	615	517
9	465*	106
2, 4, *l*		
0	2449	-2302
1	2437	2316
2	276*	-146
3	2135	1988
4	1984	1859
5	1784	-1741
6	414*	264
7	1344	-1263
8	1243	-1099
9	854	924
10	427*	-183
11	565	695
12	578	539
13	314*	-385
2, 5, *l*		
0	1231	-1386
1	352*	7
2	301*	-82
2, 5, *l*		
3	364*	76
4	1068	1098
5	389*	-65
6	414*	151
7	414*	-219
8	528	-563
9	377*	60
2, 6, *l*		
0	1344	1393
1	377*	-104
2	352*	32
3	389*	12
4	1369	-1293
5	490*	119
6	465*	-74
7	452*	-85
8	1105	986
9	389*	-58
2, 7, *l*		
0	452*	21
4	364*	-26
3, 0, *l*		
2	2839	2923
4	251*	77
6	1495	-1464
8	352*	-230
10	628	570
3, 1, *l*		
1	2826	2583
2	3052	-3160
3	1557	-1440
4	289*	-180
5	1934	-2083
6	1708	1946
7	490	449
8	440	314
9	1181	1085
10	1030	-1003
11	440*	-158
12	427*	-332
13	540	-474
14	440	458
15	264*	63
3, 2, *l*		
1	804	-717
2	703	-746
3	628	626
4	327	170
5	477	351
6	377	345
7	452	-203
8	427*	-107
3, 3, *l*		
1	1281	-1151
2	929	-923
3	1306	1163
4	214*	13
5	1281	1206
6	578	608
7	1055	-995
8	427*	-112
9	1055	-1046
10	427*	-306
11	578	591
12	377*	185
13	590	634
3, 3, *l*		
14	251*	118
3, 4, *l*		
1	314*	86
2	791	-820
3	314*	-199
4	276*	-248
5	389*	173
6	490	525
7	402*	94
3, 5, *l*		
1	641	642
2	1922	1931
3	414	-369
4	289*	-193
5	691	-645
6	1507	-1533
7	440*	171
8	427*	234
9	389*	393
10	867	963
11	327*	-116
3, 6, *l*		
1	377*	69
2	352*	144
4	327*	-64
3, 7, *l*		
1	540	528
2	1356	-1563
3	490	-378
4	377*	-15
5	427	-476
6	1193	1156
7	327*	160
4, 0, *l*		
0	2462	2248
2	226*	-267
4	1884	-1942
6	389*	332
8	1281	1380
10	490*	-87
12	917	-832
4, 1, *l*		
0	1068	944
1	867	866
2	226*	204
3	779	880
4	955	-850
5	364	-326
6	414	-324
7	414	-388
8	641	623
9	389*	52
4, 2, *l*		
0	1771	-1876
1	1871	-1773
2	239*	-128
3	2110	-1969
4	1520	1440
5	1193	1183
6	389*	265
7	1419	1582
8	741	-801
9	691	-639
10	440*	-247
11	955	-981
12	389*	418
4, 3, *l*		
0	301*	245
1	301*	-323
2	264*	117
3	301*	23
4	239*	-132
5	528	525
6	389*	-288
4, 4, *l*		
0	1130	-1076
1	1118	1107
2	289*	32
3	1319	1292
4	1017	904
5	879	-715
6	427*	-113
7	1042	-1038
8	678	-572
9	502	392
10	377*	165
11	553	586
12	301*	291
4, 5, *l*		
0	440	352
0	364*	353
1	427	446
2	327*	-95
3	452	477
4	301*	-290
4, 6, *l*		
0	1507	1608
1	389*	374
2	364*	-29
3	477	416
4	1382	-1415
5	414*	-178
6	389*	40
7	364*	-311
8	1030	972
9	276*	8
4, 7, *l*		
4	377*	248
4, 8, *l*		
1	502	-431
2	226*	-3
5, 0, *l*		
2	477	471
4	226*	-210
6	414*	-572
7	628	
8	465*	198
5, 1, *l*		
1	1243	1184
2	1507	-1600
3	1243	-1126
4	239*	-130
5	992	-949
6	1269	1424
7	741	723
8	490*	62
9	653	669
10	942	-1026
11	465*	-309
5, 2, *l*		
1	301*	256
2	1130	-1025
5, 2, *l*		
3	301*	-290
4	251*	-178
5	364*	-194
6	666	602
7	389*	199
5, 3, *l*		
1	2286	-2204
2	477	587
3	2035	1824
4	264*	123
5	1733	1777
6	440*	-490
7	1105	-1010
8	440*	-123
9	967	-1081
10	452	326
11	452	385
12	314*	64
13	427	532
5, 4, *l*		
1	440	-472
2	716	-267
3	364*	328
4	289*	-293
5, 5, *l*		
1	377*	204
2	754	814
3	389*	-341
4	314*	77
5	414*	-45
6	741	-676
7	377*	305
8	364*	-122
9	314*	-2
10	440	450
11	214*	-171
5, 6, *l*		
4	377*	85
5, 7, *l*		
1	389	436
2	603	-573
3	377	-392
4	276*	-167
5	264*	-398
6	264	467
6, 0, *l*		
0	3768	2968
2	289*	77
4	2625	-2473
6, 1, *l*		
0	703	701
1	327*	219
2	289*	-89
3	339*	353
4	615	-501
5	452*	-91
6, 2, *l*		
0	1068	-1076
1	1432	-1410
2	289*	149
3	1570	-1479
4	1068	1037
5	955	954
6	490*	-286
7	1068	1152
8	779	-823
6, 2, *l*		
9	465*	-463
10	427*	227
11	389*	-704
12	628	472
13	251*	153
6, 3, *l*		
0	352*	102
1	352*	-272
2	301*	45
3	364*	-492
4	289*	-113
6, 4, *l*		
0	364*	-59
1	553	638
2	339*	38
3	540	604
4	314*	127
6, 5, *l*		
0	389*	-491
1	389*	-134
2	364*	29
3	414*	-81
4	339*	453
6, 6, *l*		
0	917	998
1	364*	86
2	352*	113
3	352*	75
4	892	-866
5	301*	-87
7, 0, *l*		
2	339*	58
4	301*	246
7, 1, *l*		
1	452	492
2	1620	-1576
3	377*	-446
4	301*	155
7, 2, *l*		
1	666	790
2	452	437
3	603	-598
4	301*	-28
5	628	-743
6	465*	-250
7, 3, *l*		
1	867	-1022
2	339*	217
3	603	788
4	314*	-10
5	754	1000
6	465*	-78
7	452*	-515
8	414*	9
9	377*	-707
10	327*	-37
11	490	300
7, 4, *l*		
1	389*	-274
2	364*	-213
3	452	-251
4	339*	192
7, 5, *l*		
1	1030	282
2	1005	1044
3	377*	-248
7, 5, *l*		
4	352*	91
5	515	-298
6	314*	-795
8, 0, *l*		
0	992	878
2	352*	58
4	904	-799
8, 1, *l*		
0	377*	41
1	389*	255
2	352*	98
3	414*	225
4	327*	-95
8, 2, *l*		
0	427	-409
1	703	-859
2	352*	-85
3	628	-803
4	327*	338
8, 3, *l*		
0	377*	-9
1	477	-522
2	364*	-90
3	515	-549
4	339*	13
8, 4, *l*		
0	829	-811
1	528	743
2	377*	-25
3	578	676
4	766	705
5	590	-637
6	364*	44
8, 6, *l*		
0	201*	655
9, 0, *l*		
2	590	683
4	352*	1
9, 1, *l*		
2	766	-784
3	440*	-360
4	352*	-190
9, 2, *l*		
1	402*	318
2	414	-403
3	440*	-176
4	352*	-7
9, 3, *l*		
1	465	-501
2	389*	-277
3	515	556
4	364*	28
10, 0, *l*		
0	1319	996
2	389*	9
4	1080	-884
10, 1, *l*		
0	502	502
2	389*	-7
4	364*	-430
10, 2, *l*		
0	465	-474
2	389*	-12
3	452*	-263
4	414	412
11, 0, *l*		
2	402*	295
4	377*	56
11, 1, *l*		
4	377*	2
12, 0, *l*		
2	389*	19

* Indicates an unobserved reflection. The number in the F_o column in these cases represents the estimated upper limit for that reflection.

Table 2. *Final parameters*

All parameters are multiplied by 10^4. Standard deviations are given in parentheses. The refinement program used does not calculate standard deviations for the thermal parameters. The anisotropic temperature factor has the form $\exp\{(-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{23}kl+\beta_{13}hl+\beta_{12}hk)\}$.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
S	−81 (4)	1642 (5)	1221 (3)	104	152	62	2	15	31
C(1)	1783 (18)	2594 (22)	1368 (12)	154	150	36	−6	−57	122
C(2)	−999 (20)	3852 (25)	1092 (13)	177	161	42	67	−4	48
N(1)	2992 (18)	3198 (22)	1427 (12)	178	208	115	−71	−91	−7
N(2)	−1673 (18)	5265 (22)	1023 (12)	199	246	105	85	−5	146

The unobserved reflections were calculated in the final cycle and are included in Table 1. The final positional parameters are given in Table 2, and the bond distances and angles in Table 3.

Table 3. *Bond lengths and bond angles*

		σ
S —C(1)	1·736 Å	0·015 Å
S —C(2)	1·718	0·018
C(1)–N(1)	1·118	0·021
C(2)–N(2)	1·134	0·023
C(1)–S —C(2)	95·60°	0·78°
S —C(1)–N(1)	177·49	1·34
S —C(2)–N(2)	176·43	1·70

The cell dimensions reported are essentially those of Hazell. They are commensurate as well with those reported by Féher, Hirschfeld & Linke (1963), when one considers the geometry of data collection. If one examines a zero layer Weissenberg photograph rotated about [011], it exhibits two mirror planes and extinctions corresponding to screw axes along both the apparent axial rows. Without examining the first layer, it is very easy to draw the conclusion that the crystal is orthorhombic with two perpendicular 2_1 axes and the dimensions reported by Féher, Hirschfeld & Linke.

Hazell (1963) reported the space group for $S(CN)_2$ as *Cmca*, isomorphous with $Se(CN)_2$ which he refined in projection. The isomorphism was determined by comparison of zero layer Weissenberg photographs of the two compounds (Hazell, 1965). The work reported here clearly establishes the space group for $S(CN)_2$ as *Pbca*; the question then arises whether $Se(CN)_2$ is isomorphous with $S(CN)_2$ or whether $Se(CN)_2$ has symmetry *Cmca* and the structure reported by Hazell. This problem does not seem to be resolvable with the available data. The sulfur atoms in $S(CN)_2$ have very nearly *Cmca* symmetry, and if the Se atoms occupy similar positions in that structure, they will clearly dominate the scattering. Structure factors for $Se(CN)_2$ have been calculated using Hazell's cell dimensions and the position parameters given in Table 2. A comparison of these calculated structure factors with the observed structure factors reported by Hazell gives an R value of 0·136. This is almost as good as Hazell's 0·12, but does not seem at all conclusive. Refinement could improve the agreement, but since the reported data have a higher symmetry than the proposed structure, the meaning of such a refinement is dubious.

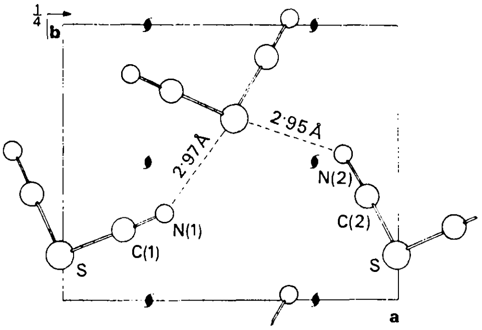

Fig. 1. Diagram showing one layer of $S(CN)_2$ molecules at $z \simeq \frac{1}{8}$. Symmetry elements are shown to indicate orientation of remaining three layers. The plane of the molecule is tilted about 7° relative to the plane of projection.

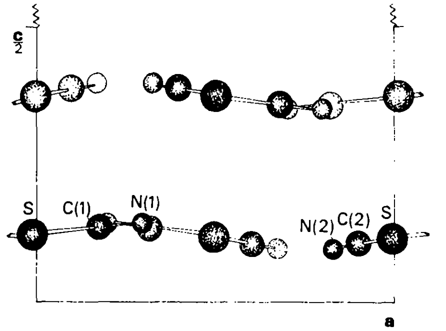

Fig. 2. The unit cell of $S(CN)_2$ from 0 to $c/2$, viewed down the b axis.

Hazell (1965) has indicated that on the basis of his data the two compounds are very probably isomorphous, and that his reported structure for $Se(CN)_2$ may thus be in error. He suggests that the error may have resulted from disorder, since in some cases streaks appeared on his photographs where spots should be if the space group is *Pbca* for $Se(CN)_2$.

This structure exhibits the familiar short nitrogen-to-heavy-atom distance which is characteristic of these cyanides. The N---S distances are 2·97 and 2·95 Å, respectively; the calculated distance using Pauling's van der Walls radii is 3·35 Å. One layer of $S(CN)_2$ molecules is shown in Fig. 1. There are four such layers in the unit cell; the symmetry elements are shown to indicate how these layers are related to one another in orientation. A view of two of these layers – half of the unit cell – is shown in Fig. 2. The molecule is planar to within one standard deviation of the parameters and exhibits C_{2v} symmetry.

A number of studies of the structure of $S(CN)_2$ have appeared recently in the literature. The most detailed treatment is that of Pierce, Nelson & Thomas (1965). The molecular parameters reported here agree very well with theirs, as shown in Table 4. Other recent studies have all been less detailed; the results are summarized in Table 4 for comparison.

The coordination at the sulfur atom is very roughly square planar, if one includes the two weakly interacting nitrogen atoms. The molecule does not exhibit the non-linear bonding at the cyanide carbon atom which has been found in $As(CN)_3$, $P(CN)_3$, $Se(SeCN)_2$ (Aksnes & Foss, 1954) and $As(CH_3)(CN)_2$ (Schlemper & Britton, 1966). It is by no means clear at present what factors are important in causing this non-linearity.

Table 4. *Comparison of molecular parameters for* $S(CN)_2$ *as determined by various methods*

Investigator	C–S bond	C–N bond	C–S–C angle	Method
Emerson	1·73	1·12	95·6°	X-ray diffraction
Pierce, Nelson & Thomas (1965)	1·70	1·15	98°20′	Infrared and microwave spectra
Rogers & Gross (1952)	—	—	105°	Dipole moment
Long & Steele (1963)	—	—	135–146°	Infrared spectra
Arnold & Rogowski (1965)	1·65	1·19	101°	Electron diffraction

Table 5. *Principal axes of thermal ellipsoids*

α,β,γ are the direction cosines relative to the crystallographic axes **a**, **b**, **c**. D is the mean square displacement of the atom in the given direction.

	α	β	γ	D
S	0·3166	0·1076	0·9426	0·0529
	0·6991	0·6451	−0·3081	0·0411
	0·6412	−0·7564	−0·1286	0·0325
C(1)	0·8405	0·4295	−0·3300	0·0726
	0·1195	−0·7413	−0·6603	0·0315
	0·5283	−0·5156	0·6744	0·0189
C(2)	0·1277	−0·6699	0·7313	0·0207
	0·9534	0·2860	0·0955	0·0676
	0·2732	−0·6850	−0·6752	0·0505
N(1)	0·4605	0·2077	−0·8629	0·1130
	0·7643	−0·5870	0·2666	0·0583
	0·4511	0·7824	0·4292	0·0404
N(2)	0·4984	−0·8053	0·3207	0·0378
	0·3990	0·5416	0·7398	0·1007
	0·7695	0·2407	−0·5914	0·0818

The direction cosines of the principal axes of the thermal ellipsoids and the mean square amplitudes of vibration are given in Table 5. The anisotropies are not large, and there does not appear to be anything unusual about the vibrations of the molecule.

Work on this project was begun at the California Institute of Technology in 1961, and the author wishes to thank the Chemistry Department of that Institute for the award of an A. A. Noyes postdoctoral fellowship at that time. The computer center at Montana State University has made its facilities freely available for the computations required in this determination.

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The Crystal Structure of $ThTi_2O_6$ (Brannerite)

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(*Received* 31 *March* 1966)

$ThTi_2O_6$, synthesized at 1610°C by solid-state reaction, crystallizes in the monoclinic system, space group $C2/m$, with the unit-cell dimensions $a=9{\cdot}822$, $b=3{\cdot}824$, $c=7{\cdot}036$ Å, $\beta=118{\cdot}84°$. It contains layers formed by Ti–O octahedra sharing edges and corners in a manner reminiscent of the anatase structure, and these are joined through thorium ions in interlayer octahedral positions. There are two Th–O distances of 2·36 Å and four of 2·35 Å, but the octahedron is flattened; two more oxygen atoms further away at 2·96 Å are probably unbonded. Ti–O distances ranging from 1·83 to 2·20 Å are normal. The structure was determined by Fourier methods and refined by several three-dimensional least-squares cycles.

Introduction

One of the gaps of appreciable magnitude in the structural inorganic chemistry of solids is listed in *Dana's System of Mineralogy* (1944, p. 745 *et seq.*) under the general title 'multiple oxides containing columbium (sic), tantalum and titanium'. These minerals contain a wide variety of substituent elements which may include the actinide elements thorium and uranium, and many of them are found in the *metamict* state. Although seeming to form crystals with extensive facial development, metamict minerals are imperfectly crystallized or even glassy substances, and it is widely believed that

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