Benghiat, V., Kaufman, H. W. & Leiserowitz, L. (1971). To be published.
Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.
Cade, P. E., Sales, K. D. & Wahl, A. C. (1966). *J. Chem. Phys.* **44**, 1973.
Cady, H. H. & Larson, A. C. (1965). *Acta Cryst.* **18**, 485.
Coppens, P. (1967). *Science*, **158**, 1577.
Coppens, P. (1968). *Acta Cryst.* B**24**, 1272.
Coppens, P., Csonka, L. & Willoughby, T. V. (1970). *Science*, **167**, 1126.
Coppens, P., Sabine, T. M., Delaplane, R. G. & Ibers, J. A. (1969). *Acta Cryst.* B**25**, 2451.
Coppens, P. & Vos, A. (1971). *Acta Cryst.* B**27**, 146.
Dawson, B. (1965). *Aust. J. Chem.* **18**, 595.
Dawson, B. (1967). *Proc. Roy. Soc.* A**298**, 264, 379, 395.
Dawson, B. & Sanger, P. L. (1967). *Proc. Roy. Soc.* A**301**, 195.
Duckworth, J. A. K., Willis, B. T. M. & Pawley, G. S. (1969). *Acta Cryst.* A**25**, 482.
Fritchie, C. J. Jr (1966). *Acta Cryst.* **20**, 27.
Hartman, A. & Hirshfeld, F. L. (1969). *Acta Cryst.* A**25**, S80.
Hirshfeld, F. L. & Rabinovich, D. (1967). *Acta Cryst.* **23**, 989.
Irngartinger, H., Leiserowitz, L. & Schmidt, G. M. J. (1970). *J. Chem. Soc. B*, p. 497.
Jensen, L. H. & Sundaralingam, M. (1964). *Science*, **145**. 1185.
Kern, C. W. & Karplus, M. (1964). *J. Chem. Phys.* **40**, 1374.
Kurki-Suonio, K. (1968). *Acta Cryst.* A**24**, 379.
Kurki-Suonio, K. (1969). *Acta Cryst.* A**25**, S85.
Löwdin, P. O. (1948). *Ark. Mat. Astr. Fys.* **35**A, no. 9.
Maslen, E. N. (1969). *Acta Cryst.* A**25**, S126.
Mason, R., Phillips, D. C. & Robertson, G. B. (1965). *Mol. Phys.* **9**, 277.
McConnell, J. F. & Sanger, P. L. (1970). *Acta Cryst.* A**26**, 83.
McLean, A. D. & Yoshimine, M. (1967). *Tables of Linear Molecule Wave Functions.* International Business Machines Corp., San José, California.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
McWeeny, R. (1954). *Acta Cryst.* **7**, 180.
Nesbet, R. K. (1964). *J. Chem. Phys.* **40**, 3619.
O'Connell, A. M., Rae, A. I. M. & Maslen, E. N. (1966). *Acta Cryst.* **21**, 208.
Rae, A. I. M. & Maslen, E. N. (1965). *Acta Cryst.* **19**, 1061.
Ransil, B. J. & Sinai, J. J. (1967). *J. Chem. Phys.* **46**, 4050.
Rietveld, H. M., Maslen, E. N. & Clews, C. J. B. (1970). *Acta Cryst.* B**26**, 693.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63.
Smith, P. R. & Richardson, J. W. (1965). *J. Phys. Chem.* **69**, 3346.
Stewart, R. F. (1969). *J. Chem. Phys.* **51**, 4569.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
Verschoor, G. C. (1964). *Nature, Lond.* **202**, 1206.
Verschoor, G. C. (1967). Ph. D. Thesis, Rijksuniv. te Groningen.
Weiss, R. J. (1964). *Phys. Letters*, **12**, 293.
Willoughby, T. V. & Coppens, P. (1969). *Acta Cryst.* A**25**, S83.

Acta Cryst. (1971). B**27**, 781

The Crystal and Molecular Structure of Methylene Dithiocyanate

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Methylene dithiocyanate, $CH_2(SCN)_2$, forms monoclinic crystals in space group $I2/c$ with four molecules in a unit cell of dimensions $a=6{\cdot}667$, $b=8{\cdot}042$, $c=11{\cdot}101$ Å, $\beta=105{\cdot}25^\circ$. The molecules are required by the space group to have symmetry 2. Three-dimensional film data were refined by least-squares methods to a conventional R index of 7·3%. The bond distances are: S–CH$_2$, 1·808 (6); S–CN, 1·677 (9); C–N, 1·194 (12) Å. The bond angles are: C–S–C, 98·2 (4); S–C–N, 176·4 (10); S–C–S, 115·0 (5)°. An intermolecular distance of 3·17 (1) Å between nitrogen and sulfur atoms on adjacent molecules suggests a weak intermolecular interaction. The intermolecular environments of sulfur and selenium atoms are compared in a number of compounds containing these atoms plus cyanide groups.

This investigation was motivated by a knowledge of the crystal structures of the isostructural trio: sulfur dithiocyanate (Feher & Linke, 1964), selenium dithiocyanate (Ohlberg & Vaughn, 1954), and selenium diselenocyanate (Aksnes & Foss, 1954). In all three of these compounds intermolecular distances shorter than the sum of the associated van der Waals radii were observed between nitrogen atoms and sulfur or selenium atoms. Each nitrogen atom appeared to participate in three intermolecular interactions, one with a bridging heavy atom, and the others with the heavy atoms in two different SCN or SeCN groups. The observed molecular symmetry of these molecules in the solid is *m*, *i.e.* both cyanides lie on the same side of the plane determined by the heavy atoms, and are approximately parallel to each other. This molecular symmetry appears to be a result of the intermolecular interactions mentioned above; we would be rather surprised to find that these molecules in the gas phase would have the same conformation. In methylene dithiocyanate the intermolecular interaction of the nitrogen atom with the bridging atom must be replaced by a van der Waals interaction (or by a C–H. . . N hydrogen bond, which seems, *a priori,* unlikely); the questions of interest are whether the same molecular conformation occurs in this molecule and what, if any, special intermolecular interactions occur.

Experimental

Methylene dithiocyanate (from the Aldrich Chemical Co.) was sublimed in vacuum to prepare single crystals suitable for X-ray diffraction. The product after sublimation had the same melting range as before sublimation, 104–106 °C. Since the crystals have an appreciable vapor pressure, they were sealed in thin-walled Pyrex capillaries to prevent sublimation during the investigation.

The unit cell and space group were determined from oscillation, Weissenberg, and precession photographs taken with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The crystals are monoclinic with $a = 6{\cdot}667$ (11), $b = 8{\cdot}042$ (13), $c = 11{\cdot}101$ (19) Å, and $\beta = 105{\cdot}25$ (25)°. (The uncertainties quoted correspond to the one part in six hundred that we regard as the normal limits to be expected in the precession method and are larger than the standard deviations calculated from the agreement among the measurements on any particular film.) A comparison of the unit-cell volume, 574 Å^3, with the molecular volume of sulfur dithiocyanate, 138 Å^3 (Feher & Linke, 1964), indicates that there are four molecules per unit cell, corresponding to a molecular volume of 144 Å^3 and a calculated density of 1·506 (5) g.cm^{-3}. The preceding conclusions were confirmed by an experimental density, measured by flotation in potassium iodide solutions, of 1·512 (8) g.cm^{-3}. Systematic extinctions, $h+k+l$ odd for hkl and l odd for $h0l$, indicate that the space group is either Ic or $I2/c$. In order to keep the needle axis coincident with a cell direction and to avoid an extremely skewed cell, the work was finished in this space group rather than converting to the more conventional Cc and $C2/c$. The morphology, observed on an optical goniometer, and a negative 'spoon test' for pyroelectricity (Bunn, 1961) suggested that the crystals are centric and that the space group should be $I2/c$; the eventual refinement of the structure confirmed this conclusion.

Determination and refinement of the structure

A needle-like crystal, elongated along **c**, approximately 0·3 mm in diameter, was selected for intensity measurements and sealed in Pyrex capillary. Multiple-film Zr-filtered Mo $K\alpha$ equi-inclination Weissenberg data were collected for the $hk0$–$hk9$ layers. Precession intensity photographs of the $h0l$ and $0kl$ layers were also collected with the same radiation. All intensities were estimated by visual comparisons with a series of timed exposures. Reflections were observable only to a spacing of approximately 0·8 Å. Of the 606 independent reflections with spacings greater than 0·8 Å, 337 were of measurable intensity, 196 were too weak to measure and 74 were not on the recorded regions of the films used. An additional 36 reflections with spacings less than 0·8 Å were also measured. Lorentz and polarization corrections were made; since μR was 0·12 ($\mu = 7{\cdot}7$ cm^{-1}), no absorption corrections were made. The Weissenberg layers were put on a common scale using the $0kl$ and $h0l$ precession data.

The above corrections as well as all the following calculations were made using programs supplied by Dr L. W. Finger of the Geology Department of the University of Minnesota and were carried out on the Control Data 1604 and 6600 Computers of the University Computer Center. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962).

The structure was determined from two- and three-dimensional Patterson and Fourier syntheses. A full-matrix least-squares refinement of the positional parameters determined from the best Fourier synthesis and of isotropic thermal parameters refined to an r value of 0·114 and an R value of 0·179.* Attempts to continue the refinement with anisotropic temperature factors for all atoms were unsuccessful in that the ellipsoid of vibration for C(1) became imaginary. It was then noted that eight of the strong reflections contributed approximately 25 per cent to r. It was assumed that these reflections were greatly affected by extinction and they were omitted in the next stage of the refinement. Also, the Weissenberg layers were rescaled; since anisotropic refinement had been carried out, there were no systematic variations in the layer scale factors, but there was a random scatter of about five per cent, which was smoothed out. At this point, with anisotropic temperature factors for all atoms, refinement converged to an r value of 0·036 and an R value of 0·094. It was then decided to make more proper extinction corrections (Stout & Jensen, 1968). A plot was made of F_c/kF_o *vs.* I_c for all reflections and a straight line fitted by eye through the resulting points. Using the slope of this line, $1{\cdot}0 \times 10^{-5}$, the F_o values were corrected according to

$$F_o(\text{corrected}) = F_o(1 + 1{\cdot}0 \times 10^{-5} I_c).$$

Using this corrected F_o list and with anisotropic thermal parameters for all atoms, the refinement converged to an r value of 0·032 and an R value of 0·071.

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* $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The numerator of r was the function refined. The weights used in the final refinement were: $w = 1$ for $F_o \leq 17{\cdot}9$; $w = (17{\cdot}9/F_o)^4$ for $F_o > 17{\cdot}9$.

A difference Fourier synthesis at this point showed peaks of 0·24 e.Å^{-3} at the expected H atom positions. (A number of other peaks, 0·2–0·4 e.Å^{-3}, occurred in the synthesis well removed from any atomic positions, so we would not regard the H atoms as having been conclusively located.) The H atoms were put in 1·07 Å from the C(1) atom and 109·5° apart, after which a final series of refinement (with the H atom parameters not refined) converged at $r=0·031$ and $R=0·069$. The final positional parameters are shown in Table 1 and the final anisotropic thermal parameters in Table 2; the observed (corrected for extinction) and calculated structure factors are shown in Table 3. Of the 196 unobservably weak reflections with spacings above 0·8 Å, nine had F_c values slightly (up to 25%) larger than the smallest observed F_o values.

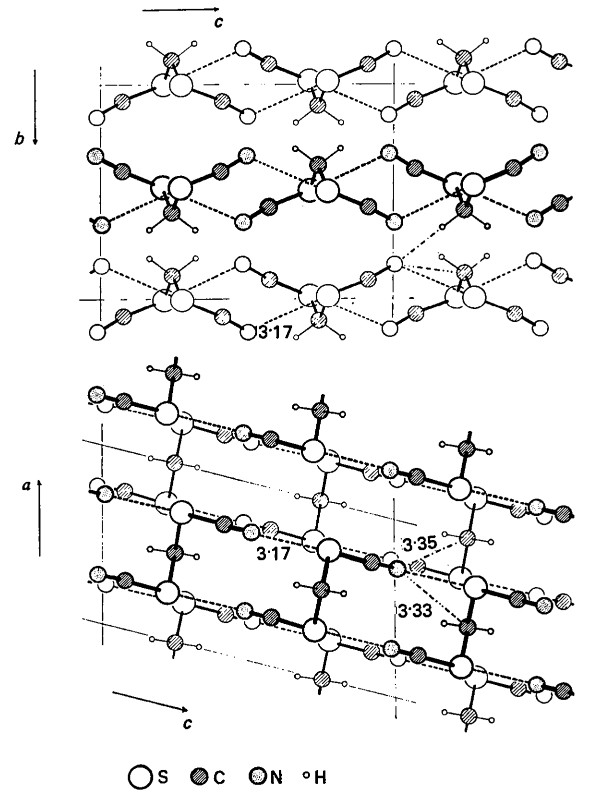
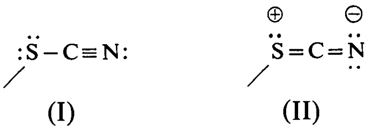


Fig. 1. Crystal structure of methylene dithiocyanate. Top: view along **a**. Bottom: view along **b**. Intermolecular distances are given in Å on the Figure. Ths hydrogen positions are assumed.

Discussion

The structure is shown in Fig. 1. The bond lengths and angles are compared in Table 4 with related values in other compounds.

The molecule in the crystal has symmetry 2. The CH_2–S bond distance of 1·81 (1) Å agrees exactly with the sum of the single bond radii reported by Pauling (1960). It is also in very close agreement with the corresponding distance reported for ethylene thiocyanate, 1·80 (1) Å. The deviation from linearity of the S–C–N angle, 176·4 (10)° is possibly real; the bending is more or less away from the methylene carbon atoms. The S–CN bond is quite short, 1·68 (1) Å. In ethylene thiocyanate Bringeland & Foss (1958) suggested that the observed S–CN distance of 1·63 (2) Å might be explained in terms of the following two structures:



(I) (II)

The structure of gaseous $S(CN)_2$ has been determined from infrared and microwave spectra by Pierce, Nelson & Thomas (1965). They, also, concluded that structure (II) was important; this conclusion was based not only on the short S–CN distance of 1·701 (2) Å, but also on nuclear quadrupole measurements, which

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

(Values in parentheses are standard deviations)

	x	y	z	B
S	0·7633 (3)	0·5143 (2)	0·7192 (2)	2·89 (5)
C(1)	1	0·3935 (10)	¾	2·67 (27)
C(2)	0·7650 (12)	0·5867 (12)	0·5779 (8)	3·77 (22)
N	0·7673 (13)	0·6470 (13)	0·4800 (7)	5·54 (22)
H	0·9931	0·3172	0·6703	2·90

Table 2. *Anisotropic thermal parameters* × 10^4

Values in parentheses are standard deviations. The anisotropic temperature factors are of the form

$$\exp\left[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)\right].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	156 (3)	138 (3)	60 (2)	34 (3)	40 (3)	12 (2)
C(1)	223 (24)	59 (12)	58 (8)	0	23 (11)	0
C(2)	168 (16)	210 (16)	62 (7)	38 (13)	10 (9)	14 (10)
N	363 (26)	299 (20)	66 (9)	99 (17)	52 (11)	74 (10)

indicated considerable double bond character for the C–N bond. However, if structure (II) is an important factor, it is not clear why the observed C–N distance of 1·157 (2) Å in sulfur dicyanide is not appreciably longer than the usual lentgh of 1·158 Å for a C–N triple bond (Britton, 1967). Since nitrogen is more electronegative than sulfur, the formal charges required in structure (II) might seem reasonable. It should be noted though that Cl–C distances in monochloroacetylene and chloromethylacetylene are 1·632 (5) and 1·637 (5) Å, whereas the paraffinic Cl–C distance is 1·767 (2) Å (Sutton, 1958). That chlorine is more electronegative than carbon makes it improbable that the resonance forms analogous to (II) are important in the acetylene compounds. It seems more reasonable, therefore, to ascribe the shortening of the Cl–C distances to the *sp* hybridization of the carbon atoms. This effect is well known for the first row elements and has been suggested for heavier elements (Bent, 1961).

Table 3. *Observed and calculated structure factors (both* × 10)

H	K	FO	FC
L = 0			
0	2	1141	1064
0	4	225	239
0	6	281	278
0	8	200	200
0	10	125	112
1	3	105	69
1	5	62	38
2	0	1335	-1401
2	2	672	-813
2	4	382	-390
2	6	318	-310
2	8	132	-139
3	1	208	163
3	3	145	108
3	5	146	113
4	0	787	868
4	2	527	513
4	4	214	209
4	6	131	130
4	8	143	143
5	1	305	-264
6	0	360	-357
6	2	323	-292
6	4	205	-196
6	6	153	-137
7	1	173	154
7	3	113	96
8	0	203	196
8	2	156	152
9	1	114	-112
L = 1			
-7	2	123	-130
-7	4	101	-113
-5	2	153	157
-5	4	133	130
-5	6	99	95
-4	1	80	79
-4	5	172	-161
-4	7	122	-124
-3	2	452	-509
-3	4	161	-166
-2	1	168	143
-2	3	295	297
-2	5	221	205
-1	2	454	469
-1	4	88	72
0	3	213	-183
0	5	230	-269
0	7	213	-213
0	9	80	-121
1	2	656	-747
1	6	109	91
2	1	272	317
2	3	326	344
2	5	173	178
2	7	82	109
3	2	135	144
4	1	77	-58
4	3	135	-128
4	5	133	-139
4	7	133	-142
5	2	108	-101
5	6	111	98
6	1	84	95
6	3	120	129
L = 2			
-9	1	147	134
-9	3	122	-112
-8	0	110	-68
-7	1	231	-207
-7	3	215	-218
-7	5	162	-133
-6	0	99	86
-6	2	202	179
-6	4	240	246
-6	6	193	161
-5	1	391	372
-5	3	310	289
-5	5	105	117
-4	0	239	-272
-4	2	377	-374
-4	4	373	-369
-4	6	249	-197
-4	8	125	-126
-3	1	396	-391
-3	3	458	-446
-3	5	221	-206
-2	2	677	645
-2	4	731	685
-2	6	321	310
-2	8	116	118
-1	3	328	328
-1	7	89	61
0	0	443	-589
0	2	1031	-886
0	4	684	-621
0	6	264	-253
0	8	190	-181
0	10	70	-99
1	1	332	-341
1	3	279	-272
1	5	151	-143
2	0	227	241
2	2	632	670
2	4	585	650
2	6	290	293
2	8	123	123
3	1	290	286
4	0	395	-403
4	2	421	-451
4	4	332	-344
4	6	163	-181
4	8	129	-131
6	0	214	224
6	2	256	258
6	4	216	244
6	6	139	145
8	0	130	-157
8	2	139	-139
8	4	122	-93
L = 3			
-7	5	103	34
-5	4	87	-85
-5	6	153	-166
-5	8	100	-121
-4	3	75	-69
-4	7	126	118
-3	4	180	173
-3	6	139	131
-2	1	150	-152
-2	3	96	-34
-2	7	116	-95
-1	2	348	351
-1	4	142	-140
-1	6	179	-194
-1	8	114	-110
0	1	113	-88
0	3	92	-78
0	5	129	113
0	7	213	219
0	9	121	138
1	2	89	-87
1	4	182	175
2	3	124	-119
2	5	130	-113
2	7	120	-113
2	9	108	-118
3	2	162	163
4	1	63	-56
4	5	93	115
4	7	141	147
L = 4			
-9	1	149	-138
-9	3	104	-114
-7	1	222	224
-7	3	220	215
-7	5	206	203
-7	7	125	114
-6	0	161	-108
-6	2	95	-93
-6	4	83	-86
-5	1	392	-404
-5	3	285	-274
-5	5	237	-246
-5	7	161	-168
-5	9	102	-73
-4	0	393	393
-4	2	238	220
-4	4	91	89
-4	6	110	107
-4	8	112	96
-3	1	426	430
-3	3	413	374
-3	5	374	404
-3	7	214	214
-2	0	469	-538
-2	2	307	-293
-2	4	309	-278
-2	6	259	-250
-2	8	85	-77
-1	3	365	-333
-1	5	315	-285
-1	7	230	-222
-1	9	91	-113
0	0	871	927
0	2	420	432
0	4	233	202
0	6	237	233
0	8	137	135
1	1	260	252
1	3	353	337
1	5	343	336
1	7	214	193
2	0	501	-522
2	2	342	-335
2	4	331	-335
2	6	276	-293
2	8	35	-83
3	1	226	-224
3	3	185	-183
3	5	133	-126
3	7	138	-135
4	0	384	411
4	2	286	293
4	4	198	205
4	6	167	184
5	3	116	113
5	5	109	114
6	0	175	-184
6	2	146	-180
6	4	174	-185
6	6	117	-145
L = 5			
-5	4	77	70
-5	6	113	131
-4	5	80	-83
-3	2	205	-180
-3	4	121	-103
-3	6	100	-99
-3	8	96	-108
-2	3	205	182
-2	5	146	140
-1	6	172	168
-1	8	174	174
0	3	48	-47
0	5	135	-195
0	7	136	-139
1	2	174	-169
1	8	93	-91
2	1	77	69
2	3	163	167
2	5	160	160
2	7	81	80
3	3	125	100
4	5	129	-130
L = 6			
-9	1	154	159
-9	3	115	119
-7	1	277	-258
-7	3	272	-243
-7	5	185	-156
-5	1	447	431
-5	3	359	370
-5	5	191	182
-5	7	113	117
-4	0	153	-127
-4	2	105	-102
-3	1	479	-452
-3	3	530	-537
-3	5	337	-323
-3	7	134	-143
-2	0	122	112
-2	2	205	203
-2	4	155	139
-1	3	535	541
-1	5	271	258
-1	7	140	147
0	0	337	-316
0	2	370	-360
0	4	119	-95
1	1	351	-353
1	3	457	-462
1	5	358	-344
1	7	130	-134
2	0	216	217
2	2	295	300
2	4	210	205
3	1	301	297
3	3	274	267
3	5	196	186
3	7	107	103
4	0	257	-269
4	2	249	-253
4	4	101	-112
5	1	98	-120
5	3	170	-160
5	5	172	-160
6	0	160	153
6	2	164	153
6	4	121	108
L = 7			
-7	2	104	88
-7	4	78	87
-5	2	86	-80
-5	4	123	-124
-5	6	113	-118
-3	2	190	180
-3	4	243	235
-3	6	93	98
-2	3	130	-122
-1	4	216	-218
-1	6	175	-167
-1	8	84	-96
0	1	98	101
0	3	68	72
1	2	139	127
1	4	252	242
1	6	82	82
2	1	121	-120
2	3	185	-181
3	4	126	-124
3	6	93	-99
4	3	86	89
5	4	97	90
L = 8			
-9	1	133	-113
-8	0	145	-136
-8	2	120	-110
-7	1	237	208
-7	3	196	162
-7	5	149	138
-6	0	253	217
-6	2	177	152
-6	4	89	50
-5	1	411	-402
-5	3	239	-217
-5	5	173	-155
-5	7	105	-121
-4	0	173	-150
-4	2	162	-140
-3	1	501	495
-3	3	320	289
-3	5	232	256
-3	7	162	156
-2	0	172	159
-2	2	144	143
-2	6	81	-43
-1	3	301	-270
-1	5	199	-169
-1	7	179	-165
1	1	414	472
1	3	285	278
1	5	222	206
1	7	155	146
2	6	90	-83
3	1	353	-379
3	3	193	-191
4	0	132	114
5	1	190	190
5	3	122	134
L = 9			
-6	3	84	-64
-5	6	98	92
-4	1	132	128
-4	3	158	138
-3	2	89	-69
-3	4	93	-71
-3	6	96	-94
-2	3	82	-78
-1	6	136	140
-1	8	146	122
0	1	122	141
0	3	151	138
0	7	60	-53
1	2	128	-119
1	4	66	-56
1	8	82	-72
3	8	89	78
L = 10			
-8	0	90	105
-6	0	214	-192
-4	0	168	154
-2	0	240	-227
0	0	133	114
0	2	73	75
0	4	98	109
0	6	76	100
2	0	121	-129
L = 12			
-6	0	205	198
-4	0	191	-175
-2	0	212	198
0	0	87	-73
0	2	138	-135
0	4	145	-145
0	6	85	-96
L = 13			
0	3	57	54
L = 14			
-6	0	126	-157
-4	0	165	159
-2	0	191	-202
0	0	132	137
2	0	121	-124
0	2	138	122
0	4	117	117

The thermal ellipsoids show no unusual features. The sulfur ellipsoid, which is the most accurately determined, has its major axis nearly perpendicular to the C–S–C plane, which seems reasonable, and the other ellipsoids do not seem unreasonable. The imaginary amplitude for the C(1) ellipsoid that was found in the early stages of refinement disappeared when the extinction correction was made.

The short intermolecular contact distances are shown in Fig. 1. There are three contact distances that are less than the sums of the associated van der Waals radii. These are the N···S distance of 3·17 (1) Å (expected van der Waals distance 3·35 Å) and the N···CH_2 distance of 3·33 (1) and 3·35 (1) Å (expected van der Waals distance 3·5 Å). The shortening of these distances relative to the expected van der Waals distances is not large and alone would not be sufficient evidence for abnormal interactions. The

Table 4. *Bond lengths and angles in* $CH_2(SCN)_2$ *and related compounds*

Compound			Reference
$CH_2(SCN)_2$	S–CH_2	1·808 (6) Å	This work
$(CH_2SCN)_2$	S–CH_2	1·80 (1)	Bringeland & Foss (1958)
$CH_2(SCN)_2$	S–CN	1·677 (9)	This work
$(CH_2SCN)_2$	S–CN	1·63 (1)	Bringeland & Foss (1958)
$S(SCN)_2$	S–CN	1·69	Feher & Linke (1964)
$Se(SCN)_2$	S–CN	1·69 (15)	Ohlberg & Vaughn (1954)
$S(CN)_2$ crystal	S–CN	1·736 (15)	Emerson (1966)
$S(CN)_2$ crystal	S–CN	1·718 (18)	Emerson (1966)
$S(CN)_2$ gas	S–CN	1·701 (2)	Pierce, Nelson & Thomas (1965)
$CH_2(SCN)_2$	C–N	1·194 (12)	This work
$(CH_2SCN)_2$	C–N	1·18 (2)	Bringeland & Foss (1958)
$S(SCN)_2$	C–N	1·21	Feher & Linke (1964)
$Se(SCN)_2$	C–N	1·13 (15)	Ohlberg & Vaughn (1954)
CH_3CN	C–N	1·157	Thomas, Sherrard & Sheridan (1955)
$S(CN)_2$ crystal	C–N	1·118 (21)	Emerson (1966)
$S(CN)_2$ crystal	C–N	1·134 (23)	Emerson (1966)
$S(CN)_2$ gas	C–N	1·157 (2)	Pierce, Nelson & Thomas (1965)
$CH_2(SCN)_2$	C–S–C	98·2 (4)°	This work
$(CH_2SCN)_2$	C–S–C	99·4 (7)	Bringeland & Foss (1958)
$S(CN)_2$ crystal	C–S–C	95·6 (3)	Emerson (1966)
$S(CN)_2$ gas	C–S–C	98·4 (2)	Pierce, Nelson & Thomas (1965)
$CH_2(SCN)_2$	S–C–N	176·4 (10)	This work
$(CH_2SCN)_2$	S–C–N	172·3 (13)	Bringeland & Foss (1958)
$S(CN)_2$ crystal	S–C–N	177·5 (13)	Emerson (1966)
$S(CN)_2$ crystal	S–C–N	176·4 (17)	Emerson (1966)
$S(CN)_2$ gas	S–C–N	175	Pierce, Nelson & Thomas (1965)
$CH_2(SCN)_2$	S–C–S	115·0 (5)	This work

geometry of the N···S interaction, discussed at greater length in the next paragraph, supports the conclusion that this interaction is more than an ordinary van der Waals interaction. Further evidence that there is some interaction stronger than the van der Waals type is that the crystals grow as needles elongated in the **c** direction, even though *c* is the longest repeat distance in the cell, and growth in this direction might be expected to be relatively slow. On the other hand, the N···CH_2 contacts are probably van der Waals contacts and not N···H–C hydrogen bonds. Although the N···CH_2 distances, 3·33 and 3·35 Å, are slightly short for van der Waals distances, the H–C···N angles, 40 and 30°, and the H···N distances (from the calculated H atom positions), 2·61 and 2·48 Å, respectively, would not satisfy the criteria for hydrogen bonding used by Donohue (1968) in his discussion of O···H–C hydrogen bonds. It should be noted that the nominally similar $S(SCN)_2$, and $Se(SeCN)_2$ molecules, in the solid, have both of their CN groups on the same side of the heavy atom plane, *i.e.* symmetry *m*, while the methylene dithiocyanate molecules have symmetry 2, which seems a more likely shape for an isolated molecule of this sort. As was pointed out in the introduction the $S(SCN)_2$, *etc.*, molecular configuration in the crystal is apparently the result of having an S or Se bridging atom, with the resultant possibility of a special intermolecular interaction to the bridging atom as well.

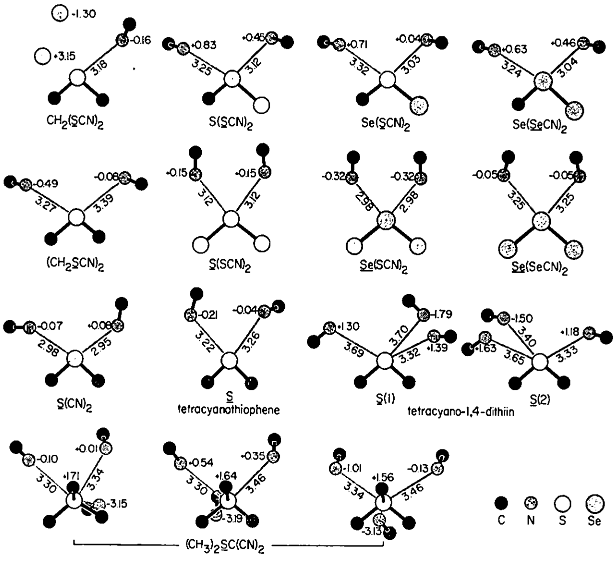


Fig. 2. The environments of S and Se atoms in compounds also containing the C≡N group. The atom considered (underlined in the formula) is shown together with the two atoms bonded to it. The neighboring N atoms in CN groups are shown at the ends of dotted lines. The numbers along the dotted lines are the S...N or Se...N distances in Å. The numbers next to the N atoms are the distances in Å above or below the planes defined by the X–S–Y or X–Se–Y groups. On the bottom line the trivalent S atom is shown with its neighbors taken two at a time. References not given previously: tetracyanothiophene, Rychnovsky & Britton, 1968; tetracyano-1,4-dithiin, Dollase, 1965; $(CH_3)_2SC(CN)_2$, Christensen & Witmore, 1969.

To the best of our knowledge there are nine compounds of completely determined structure containing divalent S or Se atoms and CN groups in the same molecule. In one of these, $K(SeCN)_3.\frac{1}{2}H_2O$ (Foss & Hauge, 1963), which is ionic, the CN groups interact with the potassium ions and not with any of the Se atoms. For the other eight compounds, as well as for $(CH_3)_2SC(CN)_2$, the environments of the S or Se atoms are shown in Fig. 2. As Foss (1967) has pointed out, something approaching square planar coordination occurs around the heavy atoms in $S(SCN)_2$, $Se(SCN)_2$, $Se(SeCN)_2$, and $S(CN)_2$, in all of which the S···N or Se···N distances are less than the expected van der Waals contact distances. However, as can be seen from Fig. 2, even in those compounds where the S···N distance is not particularly shorter than the van der Waals distance, there is still the same tendency towards the square planar environment. The two exceptions to this are: the present compound, $CH_2(SCN)_2$, where there is only one S···N contact per sulfur atom, presumably because the energy involved in these contacts is not sufficient to pull the molecules into the more strained *m* configuration that apparently would be required to form two contacts per sulfur atom; and tetracyano-1,4-dithiin, where although there are S···N contacts, in fact three per sulfur atom, there are even stronger intermolecular interactions between the electron pair on the nitrogen atom and the electron deficient region in the π system of the carbon–carbon double bond. Even in the case of the $(CH_3)_2SC(CN)_2$, if the S–C bonds are taken two at a time to define a plane, the S···N interactions are rather similar to those in the divalent compounds; in this case, however, the overall coordination is approaching octahedral rather than square planar. As Foss (1967) has discussed in detail, tellurium forms square-planar four-coordinate systems quite commonly. In view of the increasing tendency towards the four coordination as we go from S to Se to Te, it would be of considerable interest to reexamine the structure of $Se(CN)_2$ and to determine the structure of $Te(CN)_2$, as well as to look at $CH_2(SeCN)_2$ to see if the expected stronger interactions in this case would lead to a change in structure from that of $CH_2(SCN)_2$.

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References

Aksnes, O. & Foss, O. (1954). *Acta Chem. Scand.* **8**, 702, 1787.

Bent, H. (1961). *J. Inorg. Nucl. Chem.* **19**, 43.

Bringeland, R. & Foss, O. (1958). *Acta Chem. Scand.* **12**, 79.

Britton, D. (1967). *Perspectives Struct. Chem.* **1**, 109.

Bunn, C. W. (1961). *Chemical Crystallography*, 2nd ed. Oxford: Clarendon Press.

Christensen, A. T. & Witmore, W. G. (1969). *Acta Cryst.* B**25**, 73.
Dollase, W. A. (1965). *J. Amer. Chem. Soc.* **87**, 979.
Donohue, J. (1968). In *Structural Chemistry and Molecular Biology*, Ed. A. Rich and N. Davidson, p. 443. San Francisco: Freeman.
Emerson, K. (1966). *Acta Cryst.* **21**, 970.
Feher, F. & Linke, K. H. (1964). *Z. anorg. allgem. Chem.* **327**, 151.
Foss, O. (1967). In *Selected Topics in Structure Chemistry*. Ed. P. Andersen *et al.*, p. 145. Oslo: Universitetsforlaget.
Foss, O. & Hauge, S. (1963). *Acta Chem. Scand.* **17**, 1807.
International Tables for X-ray Crystallography (1962). Vol. III, p. 201. Birmingham: Kynoch Press.
Ohlberg, S. M. & Vaughn, P. A. (1954). *J. Amer. Chem. Soc.* **71**, 2649.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell Univ. Press.
Pierce, L., Nelson, K. & Thomas, C. (1965). *J. Chem. Phys.* **43**, 3423.
Rychnovsky, V. & Britton, D. (1968). *Acta Cryst.* B**24**, 725.
Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*, pp. 409–412. New York: Macmillan.
Sutton, L. E. (1958). *Interatomic Distances and Configuration in Molecules and Ions*. London: The Chemical Society.
Thomas, L. F., Sherrard, E. I. & Sheridan, J. (1965). *Trans. Faroday Soc.* **51**, 1311.

Acta Cryst. (1971). B**27**, 786

The Crystal Structure of Picryl Chloride

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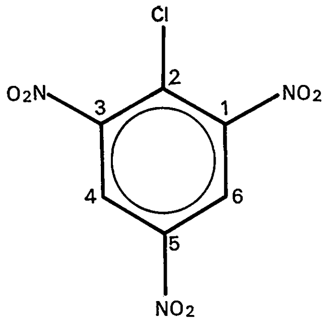
The crystal structure of picryl chloride, $C_6H_2(NO_2)_3Cl$, has been determined in separate film and diffractometer X-ray investigations. The compound crystallizes in the monoclinic space group $P2_1/a$, $Z=4$, with unit-cell dimensions $a=11{\cdot}020$, $b=6{\cdot}795$, $c=14{\cdot}964$ Å and $\beta=124{\cdot}15°$; $\varrho_{\text{meas}}=1{\cdot}797$ g.cm^{-3}, $\varrho_{\text{X-ray}}=1{\cdot}805$ g.cm^{-3} for $Z=4$. Both sets of data were refined by full-matrix least-squares methods using anisotropic temperature factors for the C, O, N and Cl atoms; H atoms were included with isotropic temperature factors in the counter data calculations. The film and diffractometer R values are 0·127 and 0·043 respectively. In most cases, the differences between the two lists of atomic parameters are less than 3σ, where σ is that of the film parameters. The two nitro groups adjacent to the chlorine atom are rotated by 33 and 81° out of the plane of the benzene ring.

Introduction

Interest in the steric interactions between nitro groups and other substituents has led to a number of structure investigations of nitro aromatics (see Holden & Dickinson, 1969, and references therein). The picryl halides (2-halo-1,3,5-trinitrobenzenes*) have been the subject of several studies during the last forty years: the structure of picryl iodide was reported by Huse & Powell (1940); Hertel & Römer (1933) proposed a packing model for picryl chloride based on a centered lattice; Kitaigorodskii (1948) reported a corrected space group and cell dimensions for the compound; and Gol'der, Zhdanov & Umanskii (1953) published a partial structure. In the latter determination, only an outline of the picryl chloride skeleton in a projection was reported and the positions of two of the oxygen atoms were not specified.

Our own work on picryl chloride, 2-chloro-1,3,5-trinitrobenzene,* has spanned a period of ten years and the results of two separate determinations, one with film and another with counter data, are reported herein. A preliminary account of part of this work has been published (Gluyas & Harris, 1959).



Experimental

Commercially available picryl chloride (Eastman Kodak Co.) recrystallized from a chloroform–carbon tet-

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* The present *Chemical Abstracts* numbering scheme for picryl halides places the halogen on C(2).