The Crystal Structure of Xanthane Hydride

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The crystal structure of xanthane hydride has been determined by analysis of three-dimensional data from copper X-radiation. The y and z coordinates were determined from a Patterson projection, and the x coordinates were then determined by the use of the projected bond lengths and twenty-five low order $1kl$ reflections. The coordinates of all nine atoms and the anisotropic temperature parameters for the seven heavy atoms were refined by the method of least squares. The final R index was 0·069.

The xanthane hydride molecule is essentially planar and is bound to neighboring molecules by N–H–N and N–H–S hydrogen bonds. Both hydrogen atoms were found to be on the non-ring nitrogen atom. The bond lengths are not significantly different from those found in similar structures.

Introduction

Xanthane hydride, $C_2H_2N_2S_3$ (I), is a member of a group of five-membered cyclic disulfides, some of whose structures have been reported (Foss & Tjomsland, 1958; Kehl & Jeffrey, 1958; Hordvik, 1960). This structure determination was initiated at the Rice Institute in 1957 with the hopes of obtaining accurate values for the bond lengths and angles and illuminating the aromatic character of the compound.

(I)
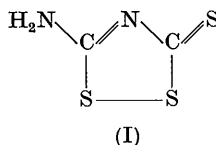
While this investigation was in progress, Hordvik (1961) published a solution of the structure in the [100] projection, which he obtained by direct methods. No three-dimensional work was mentioned.

Experimental

Xanthane hydride was prepared by adding $7M$ ammonium thiocyanate to concentrated hydrochloric acid (Zappi, 1930, 1931; Hantzsch & Wolvekamp, 1904). Thin yellow crystalline needles, elongated along a, were formed by allowing the solution to stand overnight. Intensity data for the $0kl$, $1kl$, $2kl$, and $3kl$ layers were collected by the multiple-film equi-inclination Weissenberg technique with Cu $K\alpha$ radiation. Because of instrumental difficulties it was impossible to collect the $4kl$ data by the equi-inclina-

tion technique. General-inclination photographs were taken of this layer, but the spots were distorted and diffuse and the photographs were of inferior quality. The final structure derived shows agreement for this layer ($R=0·14$) that is poor in comparison with the agreement for the other layers, so these data were not included in the parameter refinement.

The intensities were estimated visually by comparison with a prepared scale and were corrected for Lorentz and polarization factors. No absorption corrections were made. Ten of the strong, low order reflections seem to be affected by extinction, and were omitted from the R factor and the least-squares refinement. Of the 1227 independent reflections within the copper sphere, 895 are on the first four layer lines; of these, 699 were strong enough to be measured.

The unit-cell dimensions, summarized in Table 1, were determined from Straumanis-type single-crystal rotation photographs about the a and b axes. The measured spacings of six $h0l$ and seven $0kl$ high-angle

Table 1. *Unit-cell parameters of xanthane hydride*

	This investigation*	Foss (1956)†
a	$4·1030 \pm 0·0006$ Å	$4·05$ Å
b	$10·5675 \pm 0·0009$	$10·59$
c	$12·8012 \pm 0·0012$	$12·78$
β	$98° \, 5' \pm 1'$	$97°$

* Estimated errors are three times the standard deviations given by the least-squares analysis. These errors probably indicate only the precision of the data. A change of one degree in temperature might well cause a change in axial lengths of the order of magnitude of their estimated error; accordingly, in the absence of a temperature control, the reported errors are of dubious significance.

† Errors estimated to be about 0·5%.

reflections were used as input to a least-squares treatment. The output parameters are in fair agreement with those of Foss (1956), which are also listed in Table 1. The absence of $h0l$ reflections with l odd

and $0k0$ reflections with k odd indicates that the space group is $P2_1/c$.

The density of the crystals as measured by the flotation method is $1.81_0 \pm 0.005$ g.cm^{-3}. The density calculated for xanthane hydride, assuming four molecules per unit cell, is 1.816 g.cm^{-3}.

Determination of the structure

The first attempt at solving the structure was by use of the $0kl$ data. The Patterson projection along the a axis is shown in Fig. 1. The interpretation of this projection was reasonably straightforward, and tentative y and z parameters for the seven heavy atoms were chosen. The structure factors calculated for this trial structure were in good agreement with the observed values, and after two least-squares refinement cycles the R index was 0.15.
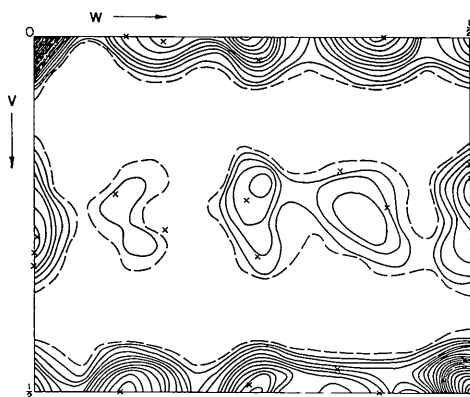

Fig. 1. The Patterson projection in the [100] direction. Contours at arbitrary but equal intervals. Crosses mark positions of sulfur–sulfur interactions for the final structure.

From the projected bond lengths calculated from the y and z coordinates, two possible three-dimensional orientations of the molecule were established. Only the choice of the correct orientation and the position along the a axis were then necessary. Accordingly, structure factors were calculated for twenty-five low-order $1kl$ reflections using the parameters for each of the two possible orientations and allowing the molecule to migrate through the cell with increments of 0.1 in x. Only one of the orientations showed any reasonable agreement with the observed values. The R index for this orientation varied from a maximum of 0.90 to a minimum of 0.45 for two adjacent positions; for an intermediate position R was 0.42. Least-squares shifts were applied to the parameters for the next cycle, which included approximately one-half of the $1kl$ data and used weights proportional to $1/F_o$. The R index was now 0.30, and for the next cycle one-fourth shifts were allowed. In the next two cycles all of the $1kl$ data were included with the same shift factor and the same weighting. The R indices for these two cycles were 0.15 and 0.09.

Attention was now turned to the complete three-dimensional data.

Refinement of the parameters

The structure was refined by a series of structure-factor least-squares cycles. The atomic form factors were those of Tomiie & Stam (1958) for sulfur, McWeeny (1951) for hydrogen, and averages of those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and Hoerni & Ibers (1954) for carbon and nitrogen. The calculations were carried out on a Burroughs 220 computer with a program written by Dr Richard E. Marsh of these laboratories. This program will accept and optimize ten parameters per atom: three positional coordinates, six temperature parameters, and a population scale factor. The program neglects interatomic interactions; for an individual atom the cross terms between the scale and temperature parameters and between the x and z coordinates are collected. The quantity minimized is $\Sigma w(\Delta F^2)^2$. The weight, $\sqrt{w}$, used throughout the complete refinement was $1/F_o$ if $F_o \geq 4F_{min}$ and $1/(F_o.4F_{min})^{\frac{1}{2}}$ if $F_o \leq 4F_{min}$, where F_{min} was taken as 4.11. Unobserved and very weak reflections whose intensities were estimated as being less than a certain value were omitted from the R index, but those whose calculated structure factors were greater than the estimated maximum possible values were included in the least-squares.

In the initial cycles only the coordinates and isotropic temperature parameters of the seven heavy atoms were adjusted. Refinement was continued until the shifts were no longer significant in comparison with the standard deviations; R had dropped to 0.09. At this point anisotropic temperature parameters were introduced for all seven heavy atoms. The refinement was continued until the shifts were again insignificant in comparison with the standard deviations. The R index was 0.071. The positions of the hydrogen atoms were then calculated, assuming a planar amine group with N(2)–H distances of 1.0 Å. The hydrogen atoms were assigned fixed isotropic temperature parameters of 3.0 Å^2. During the succeeding least-squares cycles both hydrogen atoms seemed to drift away from N(2) along the directions of the apparent hydrogen bonds, raising the possibility of tautomeric forms. At this juncture each of the hydrogen atoms was replaced by two separated half hydrogen atoms. This replacement, however, had little effect on the sum of the weighted residuals or on the R index. Indeed, during succeeding cycles the half hydrogen atoms tended to merge and their final least-squares positions were within a standard deviation of each other and of the original single positions. Single hydrogen atoms were, therefore, re-entered.

At this stage the R index was 0.069, and no shift was greater than one-third of its standard deviation. The final parameters and standard deviations of the

Table 2. *The final parameters and their standard deviations*

All values are multiplied by 10^4. The temperature factors are of the form:

$$T_i = \exp -(\alpha_i h^2 + \beta_i k^2 + \gamma_i l^2 + \delta_i hk + \varepsilon_i hl + \eta_i kl)$$

Atom	x	σ_x	y	σ_y	z	σ_z
S(1)	2751	(7)	1513	(2)	0517	(2)
S(2)	5296	(7)	1601	(2)	2014	(2)
S(3)	8741	(7)	3812	(2)	2963	(2)
N(1)	5389	(22)	3781	(6)	1024	(8)
N(2)	2381	(22)	3601	(6)	−0637	(8)
C(1)	6479	(21)	3189	(7)	1921	(7)
C(2)	3559	(26)	3121	(7)	0273	(8)

Atom	α	σ_α	β	σ_β	γ	σ_γ	δ	σ_δ	ε	σ_ε	η	σ_η
S(1)	532	(25)	46	(2)	35	(2)	−96	(10)	27	(8)	−2	(3)
S(2)	379	(22)	35	(2)	27	(1)	−22	(9)	36	(7)	11	(3)
S(3)	420	(24)	46	(2)	39	(2)	33	(10)	−51	(8)	−6	(3)
N(1)	499	(79)	51	(8)	24	(5)	−21	(36)	−22	(26)	6	(10)
N(2)	568	(82)	51	(8)	25	(5)	−81	(36)	−45	(28)	6	(10)
C(1)	66	(74)	27	(8)	37	(6)	−25	(30)	74	(28)	6	(10)
C(2)	401	(92)	42	(9)	26	(6)	−27	(38)	58	(32)	−13	(10)

Table 3. *Comparison of parameters for Hordvik (1961) and for this investigation*

	Hordvik*		This investigation	
Atom	y	z	y	z
S(1)	0·151	0·051	0·151	0·051
S(2)	0·158	0·199	0·160	0·201
S(3)	0·382	0·299	0·381	0·296
N(1)	0·375	0·105	0·378	0·102
N(2)	0·359	−0·055	0·360	−0·064
C(1)	0·323	0·190	0·319	0·192
C(2)	0·313	0·030	0·312	0·027

* The values reported by Hordvik are for a different equivalent position in the unit cell, and have been re-evaluated for presentation here.

Table 4. *Parameters of hydrogen atoms*

Isotropic temperature factor $B = 3·0$ Å²

Atom	x	σ_x	y	σ_y	z	σ_z
H(1)	0·281	0·032	0·480	0·009	−0·076	0·013
H(2)	0·047	0·032	0·284	0·010	−0·121	0·013

heavy atoms are shown in Table 2. Table 3 gives a comparison of the values of Hordvik (1961) for the y and z coordinates with those of this investigation. The parameters of the hydrogen atoms are given in
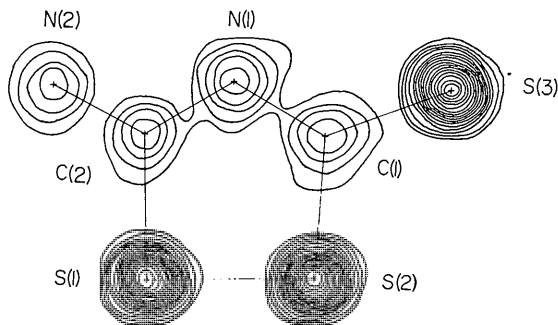
Fig. 2. The electron density in the least-squares plane of the molecule. The lowest contour is drawn at 2 e.Å⁻³, and the interval between contours is 2 e.Å⁻³.

Table 4. The observed and final calculated structure factors are listed in Table 5. The electron density in the plane of the molecule is shown in Fig. 2 and the corresponding difference Fourier synthesis is shown in Fig. 3.
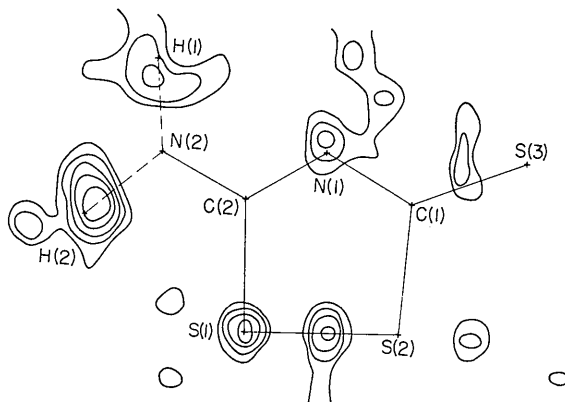
Fig. 3. A plot of the difference Fourier syntheses in the least-squares plane of the molecule. The lowest contour is drawn at 0·2 e.Å⁻³ and the interval between contours is 0·1 e.Å⁻³.

Discussion

The xanthane hydride molecule is essentially planar, and is hydrogen bonded to the neighboring molecules through N–H–N and N–H–S hydrogen bonds. These bonds, of length 2·98 and 3·35 Å, are indicated in the packing diagram of Fig. 4. The intramolecular bond lengths and angles between the heavy atoms are given in Table 6 and shown in Fig. 5; those involving hydrogen atoms are listed in Table 7. The estimated standard deviations of these bond lengths, derived from the least-squares analysis, are 0·004 Å for S–S, 0·009 Å for C–S, and 0·012 Å for C–N; the standard deviations for the bond angles are approximately 0·1° for the S–S–C angles and 0·2° for the other angles. For the N–H bond lengths the estimated standard deviation is 0·14 Å.

Table 5. *Observed and calculated structure factors*

The three columns in each group contain the values, reading from left to right, of l, $100|F_o|$, and $100\,F_c$. Reflections marked by † were omitted from the R index and the least-squares calculation

(Each group lists: l, 100|Fo|, 100Fc)

00l
```
 2  1054  -1394
 4  3733   4057
 6  1060   -896
 8  7079  -7711
10  2571   2935
12  4249  -4880
14   645    760
16   650    665
```

01l
```
 1  1070    959
 2  3840  -5276†
 3  3125  -3308
 4  1543  -1435
 5  5215   5915
 6  3542  -3703
 7  3526  -3542
 8  1010   -896
 9  4480    -16
10  4513   -486
11   951  -1015
12   795  -1002
13  1596  -1515
14  1368   1289
15  1570   1663
16   448    341
```

02l
```
 0  4666  -6988†
 1   933    884
 2   427   -306
 3  4011  -4227
 4  1806  -1724
 5  4315  -4385
 6   669   -616
 7  2732  -2761
 8  2085   1993
 9   552   -397
10  4519   -273
11  2232   2365
12  1222   1296
13  2269   2265
14  4555     36
15  1291   1312
```

03l
```
 1  2140  -1890
 2   653    477
 3  3329   3125
 4  3156  -3218
 5  5391  -5321
 6  3196   2838
 7  4413   4743
 8   248   -821
 9   565    356
10  4526    301
11  1503   1430
12  2645    155
13  1878   1935
14  4532   -419
15  2068  -2090
```

04l
```
 0  6910 -13537†
 1  3980   3413
 2  1678   1622
 3  4342    272
 4  1855  -1776
 5  2346   2016
 6  1489   1198
 7  1237   1221
 8  4650   5042
 9  1754  -1739
10  1891  -2029
11  4653    491
12  3420   3193
13  2225  -2276
14   640   -773
15   434   -413
```

05l
```
 1   465   -640
 2  3513   3516
 3  1157   1154
 4   988    739
 5  3399  -3417
 6  3453   3214
 7   650    749
 8  4511    299
 9  4529   -356
10  4537    285
11  4464     -5
12  4609    553
13   801    835
14  1550  -1562
```

06l
```
 0  7565   7059
 1  1626  -1410
 2   535    490
 3  2757   2601
 4  2064   1924
 5  2445   2127
 6  4490    164
 7  2252   1972
 8  3547  -3668
 9  1455   1448
10  4650    161
11  1797  -1745
12  2030  -2098
```

07l
```
 1  2777   2510
 2  2967  -3032
 3  1253  -1247
 4  3308   3346
 5  3665   3771
 6  5297  -5565
 7  2800  -2755
 8  1022   1102
 9   690   -618
10   513   -629
11   750   -879
12   643   -701
13  2045  -1847
```

08l
```
 0  2575   2373
 1  3634  -3884
 2   567   -497
 3   686   -553
 4  4511   -341
 5  2610  -2697
 6  1150  -1156
 7  2576  -2639
 8  1093  -1130
```

(08l cont.)
```
 9  1496   1726
10  4530    568
11  1047  -1005
12   602   -551
13  2065   2095
```

09l
```
 1  1388  -1448
 2   662   -415
 3   667   -500
 4  1261  -1184
 5   671    662
 6  4532    -53
 7   699    796
 8  4610   -213
 9   643    611
10  4511    165
11   541    474
```

0,10,l
```
 0  2436  -2592
 1  2479   2519
 2   809   -795
 3  3350  -1483
 4   526   -487
 5  4517     56
 6   565    611
 7  4531    178
 8  2210   2105
 9  1718  -1678
10   925    657
```

0,11,l
```
 1   876   -927
 2  2306   2242
 3  4603     94
 4  1951  -2031
 5  1169  -1301
 6  3310   3866
 7  4490    383
 8   924  -1062
 9   594    484
```

0,12,l
```
 0  4542    446
 1  2309   2393
 2  4530    -70
 3   642    547
 4   490    503
 5  1566   1544
 6   412    321
 7  1833   1860
```

10l
```
 2  1749  -1718
 4  1111  -1213
 6  3956  -3870
 8  4471   -193
10  2132  -2483
```

11l
```
 1  3024  -3038
 2  1970  -2108
 3  2782  -2520
 4  4213  -4566
 5  3374  -3186
 6  5853   6475
 7  1801  -1760
 8  1504  -1678
 9  2011   2068
10  4090   4351
```

11l
```
 1  2954   5435†
 2  4897  15193†
 3  1470   1491
 4  3012  -3380
 5  2176   2176
 6  3005   2981
 7  1831   1888
 8  3167  -3244
 9  4470   -380
10  3178  -3249
11  4644    201
12  1767   1631
13  1503  -1452
14  2168  -2184
15  1254  -1276
```

12l
```
 0  3467   3443
 1  3969   4242
 2  3406  -3320
 3  6625  -7656†
 4  3785   3657
 5  3578   3325
 6  1275   1153
 7  1684   1850
 8  4480   -129
 9   602   -698
10  1360   1377
11  3614   3282
12  1336  -1209
```

(12l cont.)
```
 3  1936   1684
 4   677   -785
 5  4712   4746
 6  2324   2266
 7  1034    942
 8  1373  -1487
 9  1336  -1464
10  1908   2010
11  1110   -956
12  4610    -63
```

13l
```
 1  4344  -4357
 2  5121   5252
 3  4182  -3946
 4  1907  -1910
 5  1683  -1630
 6   390    494
 7  3803  -3798
 8  2112  -2031
 9   942    953
10  1626  -1653
11  4652    581
12  1161   1060
13  1602   1439
14   682   -827
15  2391   2367
```

14l
```
 0  1820   1815
 1   676   -547
 2  2526   2344
 3  1024    639
 4  1670  -1532
 5  4421    172
 6  2325   2344
 7  1468  -1352
 8  4509     65
 9  4529    283
10   709    881
11  1263  -1336
12  4587   -190
```

14l
```
 1  3003  -2642
 2   652   -763
 3  3148   1577
 4   904   -789
 5  4392   -214
 6  3653  -3479
 7  1045    891
 8  4482   -393
 9  2452   2618
10  4588     78
11  4533   -241
12  4632    201
13  1508   1491
14   942    648
15  4411   -315
```

15l
```
 0  2071   1967
 1  1052    924
 2  1551   1546
 3  2247   2183
 4  3040   3303
 5  4454   -293
 6  4977  -5300
 7  2438   2417
 8   772    854
 9  1986  -2051
10  3710  -3549
11   876    778
12  1220  -1371
```

15l
```
 1  2437  -2277
 2  7685  -9033†
 3  2997   2883
 4  2436   2618
 5  2002  -1937
 6  2008  -2058
 7  1309   1267
 8  3095   3347
 9  1214  -1121
10  2810   3169
11  1107  -1310
12  1077  -1064
13   857    899
14  1830   1876
```

16l
```
 0  4610  -4381
 1  1705  -1813
 2  2142   2254
 3  4755   4672
 4  4505  -4514
 5  2570  -2484
 6  1530  -1480
 7   833   -787
 8  4532    422
 9  4647    133
10  2715  -2218
11  2004  -2017
12  2400   2291
```

16l
```
 1  3140  -3022
 2  3105   2812
 3   639   -652
 4  1610   1608
 5  1380   1299
 6  4487   -281
 7  3779  -3531
 8  3905   4082
 9  2336   2170
10  1988  -1739
11  4527   -347
12   946   1049
13   884    948
14   725   -718
```

17l
```
 0  2406  -2141
 1  2141  -2167
 2   701   -624
 3  1988  -2083
 4  1467  -1575
 5  3916  -4154
 6  1128   1173
 7  1042   -909
 8  1140   1061
 9  4512    489
10  4583      2
11   653    637
12   927   1077
```

17l
```
 1   975   1035
 2   587    579
 3  2785   2824
 4  4490      0
 5  1419   1359
 6   846    927
 7  2585   2666
 8  4533   -160
 9  4645    393
10  4585    -90
11  4585   -426
12   593   -460
13   549   -563
14  4304   -403
```

18l
```
 0  1828   1860
 1  4511    146
 2  2518  -2727
 3  1468  -1454
 4  3301   3569
 5  4533     47
 6  4651   -567
 7  1907   1747
 8  4621   -252
 9  4580    -26
10   931   1066
11  1841   1975
```

18l
```
 1  3377   3419
 2   948  -1035
 3  4514    300
 4  4519   -619
 5  4523    455
 6  2326   2490
 7  4651     78
 8  2201  -2118
 9  2451  -2400
10   954    962
11  4526    -15
12   881   -842
```

19l
```
 0  1080  -1129
 1  4533    197
 2  4534   -575
 3   604   -705
 4   605   -562
 5  3559   3132
 6  1806   1754
 7  1839  -1957
 8  4565    326
 9  2163   2115
10  1061   1252
```

19l
```
 1  2009   2084
 2  2661   2628
 3  3988  -4230
 4   604   -712
 5  1209   1451
 6  4642   -100
 7  2821  -2757
 8  2199  -2021
 9  4568    446
10  1784  -1650
11  1495   1459
```

1,10,l
```
 0  2107   1961
 1  4642    561
 2  1247  -1165
 3  1444  -1384
 4  4398   2184
 5  1281   1206
 6   795    664
 7  4533   -468
 8  4480   -441
```

1,10,l
```
 1  4531   -483
 2  1744  -1990
 3   565    708
 4  1052   -906
 5  1041   -879
 6  4602   -182
 7  1897   1860
 8  2186  -2220
 9  4480    345
10  1155   1358
```

1,11,l
```
 0  2008   2011
 1  1007    801
 2  4583    282
 3  1476   1489
 4  1163   1222
 5  1271   1319
 6  1194  -1187
 7   797    821
```

1,11,l
```
 1  4602   -184
 2   675   -628
 3   664   -574
 4  4573    402
 5  1203  -1154
 6  4522   -372
 7  4481   -409
 8  1115   1309
```

1,12,l
```
 0  1816  -1933
 1   575    443
 2  1922   2142
 3   533    682
 4  2470  -2642
```

1,12,l
```
 1  1664  -1640
 2  1769   1737
 3  1078  -1055
 4   782    700
 5  4442   -279
 6   887  -1163
```

20l
```
 2  5414  -7802†
 4  4836   4884
 6  1202  -1166
 8  4323   4403
10  4506   3762
```

20l
```
 4  6778  -6828
 6  4272   3778
 8  2598  -2389
10  4293   4197
12  1617   1022
14   985   -985
```

21l
```
 0   881   1290
 2  2445  -2996
 3  4439   -253
 4  4034   4283
 5  1708   1659
 6  4489     -4
 7  1513  -1540
 8  1750   1861
 9  2048   1894
10  4664   -136
11   809   -914
```

21l
```
 2  1353  -2137
 3  3085  -3027
 4  1511   1783
 5  2076   2206
 6  4399   -181
 7   441    243
 8  2800   2782
 9  4868   -263
10   869    699
11  2215   2229
12  4688   -623
13   899   -754
14  4581    116
15  1547   1503
```

22l
```
 0  4259    160
 1   270    758
 2  1965   1932
 3  3148   3078
 4  1421  -1214
 5  3792   4189
 6   634   -427
 7  2500  -2555
 8   708   -612
 9  1635   1714
10  1438  -1538
11  2059  -2083
```

22l
```
 1  2266  -2700
 2  1686   1731
 3  5369   7958†
 4  1298   1453
 5  1730   1663
 6   595   -533
 7  1929   2015
 8   680    612
 9  1158   1585
10   851   -823
11  2552  -2469
12  4681     62
13  4639    441
14  4570     53
```

23l
```
 0  2139   2072
 1  2940   2821
 2  2861  -2993
 3  1094   1080
 4  1119   1182
 5  2639  -2576
 6   740    667
 7  1574   1812
 8   804   -707
 9  2062  -2329
10  1263   1103
11   620    466
12  1912  -1509
```

24l
```
 0  4386    359
 1  2049   2159
 2  4453   4877
 3  2504  -2429
 4  4868  -2867
 5  4511   -581
 6  1097   1092
 7  4685   -167
 8  3106  -3123
 9   777   -717
10  2117  -2105
11  1479   1565
12  1000   1127
```

24l
```
 1  1357   1349
 2  1354   1380
 3  2888  -3115
 4  4085   4163
 5  4672  -2265
 6  2715  -2798
 7  4508    181
 8  1122   1246
 9  2101  -2360
10  3840  -3458
11  2821   2278
12  1256  -1111
13  4594    154
14   634    677
```

25l
```
 0   932   -706
 1  2538   2560
 2  4468    599
 3  5007  -2904
 4  3591  -3742
 5  4536    152
 6  4560    262
 7  4693    280
 8  1818  -1774
 9  1020   -962
10  4618    310
11  1231   1179
12  1523   1549
```

25l
```
 1  1576  -1534
 2  1677   1516
 3  1109   1053
 4  2764  -2637
 5   988   1020
 6  4514    112
 7  1147  -1155
 8  2565  -2660
 9  2393   2546
10   947    729
11  4659   -199
12   952   1032
13  4553    307
```

26l
```
 0  4494   -442
 1  2278  -2265
 2  3392  -3490
 3  1649  -1534
 4  1635   1547
 5  2677  -2780
 6  1147   1127
 7  1542   1526
 8   754    746
 9   865   -684
10  2429   2866
11   765    843
```

26l
```
 1  1443   1231
 2  3229  -3304
 3  2726  -2661
 4  1517  -1316
 5  4550   -335
 6  1399   1314
 7  1715  -1661
 8  4567   -610
 9  4692     83
10  2284   2216
```

27l
```
 0  2182  -2208
 1  2298  -2256
 2  3120   3135
 3  4558     43
 4  1308   1288
 5  1770   1866
 6  1108  -1165
 7   760   -720
 8  2240   2461
 9  2297   2093
10  1770  -1736
```

27l
```
 1  4535    308
 2  2643  -2718
 3  3580  -3573
 4  2776   2947
 5   874    756
 6  4566    -69
 7  4693    -82
 8   779   -724
 9  4671   -132
10  1433   1485
11  1885   1875
12  1237  -1333
```

28l
```
 0  4566   -456
 1  1098  -1127
 2   778   -725
 3  3493   3319
 4   709    617
 5   695    646
 6   623   -802
 7   955    851
 8  1561   1533
 9   570    558
```

28l
```
 1  1693  -1406
 2   713    611
 3  2169   1730
 4  1581  -1465
 5  2461   2795
 6   634    980
 7  4560   -332
 8  4660     81
 9  2494   2431
10  1446   1202
11  1690  -1626
```

29l
```
 0   747    778
 1   859  -1006
 2   761   -946
 3  2770   2703
 4  1480   1326
 5  1519  -1386
```

29l
```
 1  1452   1330
 2  2689    237
 3  1555   1620
 4  1348   1149
 5  2583  -1258
 6  4661     60
 7  1312   1312
 8  1853   1905
 9  2243  -2146
```

2,10,l
```
 0   604    444
 1  2383   2160
 2  2844   1866
 3   758   -859
 4  4589   -196
 5  1141   1218
 6  1344  -1301
 7  1190  -1020
```

2,10,l
```
 1  4654    214
 2  2647   2549
 3  4647    543
 4  4632     38
 5   911   -910
 6   841   -806
 7  1169   1203
```

2,11,l
```
 0  1565   1547
 1  1132   1163
 2  1741  -1547
 3   956   -957
 4  1359  -1384
```

2,11,l
```
 1  4575   -100
 2  1445   1570
 3   930    920
 4  3152  -3072
 5   958    954
```

30l
```
 0  1539  -1969
 1  4020   4218
 2  4030    922
 3  4580    226
 4  1671   1527
```

30l
```
 4  1559  -1137
 6  1230   -833
 8  4566    511
10  2598  -2506
12   962   1012
```

31l
```
 0  3574   4282
 1  4359   -341
 2  4263    105
 3   646    694
 4  1422  -1594
 5  3705  -3985
 6   491   -537
 7  4534    236
 8  1162   1391
 9  1161  -1276
10   821   -505
11  4705     96
12  1972   1668
13  1447   1310
```

32l
```
 0   417   -302
 1  1442   1643
 2  1423  -1400
 3  1761  -1844
 4  4536    247
 5  1931   2094
 6   871   -964
 7  1686  -1478
```

32l
```
 1  1497  -1279
 2  4352    -24
 3   704   -493
 4  4531   -431
 5  3606  -3262
 6   873    800
 7  2613   2907
 8  4576   -339
 9  4784    594
10  4784    936
11  1962   1852
12  4645   -184
13  1384   1226
```

33l
```
 0  2543   2363
 1  4566   -133
 2   680   -734
 3  3998  -4056
 4   980    936
 5  5372   1566
 6  1317   1343
 7  3453  -2808
 8  4699   -654
 9   833    822
```

33l
```
 1   960   1069
 2  4427     84
 3  1240  -1226
 4  4475      1
 5  6003   5848
 6   771   -691
 7  4566     -7
 8  1037   1181
 9  1374   1436
10  4587   -496
11  4681    569
12  1353   1214
13  2230  -2413
```

34l
```
 0  2204   2203
 1  3215  -3132
 2  2903  -2797
 3   820    799
 4  1088   -997
 5  4595   -349
 6  4594    465
 7  4714   -427
 8  1589  -1504
 9  1575   1360
10  2442   2072
```

34l
```
 1   776   -927
 2  1470  -1833
 3  1735   1739
 4  1617   1576
 5  4544    519
 6  4567    649
 7  1851  -2007
 8  4724    875
 9  4594   -241
10  2312   2148
11  2349  -2381
```

35l
```
 0  3645  -3951
 1  4559    467
 2  4570    169
 3   871   -843
 4  4596    359
 5  1060    978
 6  4589   -110
 7  4669     23
 8  3189   2803
```

35l
```
 1  2138  -2281
 2  4546    132
 3  4651    197
 4  2699   2045
 5  4579   -480
 6  4588   -110
 7  4596   -270
 8  1170  -1350
 9  4707    634
10  4671     67
11  1026  -1054
12  1988  -1959
```

36l
```
 0  4582    -49
 1  1084   1101
 2  2473   2627
 3  1135    982
 4  4723   -529
 5   955   -996
 6  1740   1711
 7  1805   1762
 8  4586    -40
 9   657   -622
```

36l
```
 1  1873   1912
 2  4680     19
 3   661   -775
 4  4589    395
 5  2237   2322
 6  2248  -2266
 7  4593   -360
 8  4707    570
 9  4676   -431
10  1229  -1038
```

37l
```
 0  4596     15
 1  1077   1125
 2   850    987
 3  2658   2582
 4  1376  -1454
 5  4679   -352
 6  1383   1848
 7  1602   1582
 8  1408  -1287
```

37l
```
 1  4596   -107
 2  4597     26
 3   947    759
 4  1466  -1540
 5  3159  -2885
 6  1327   1203
 7  4693   -403
 8  4665   -547
 9   618   -709
10   552    546
```

38l
```
 0  1306  -1417
 1  2591   2453
 2  4691    347
 3  1043  -1071
 4   971    917
 5  4611    -68
 6  1498  -1406
```

38l
```
 1  4715    478
 2  2155   1219
 3  1675  -1635
 4  1469  -1345
 5   987   -874
 6  4669    444
 7  1150   1223
 8  4591   -823
 9   599   -754
```

39l
```
 0  1789   1806
 1  1338  -1295
 2  4633    461
 3  4600   -409
 4  4561   -249
 5  4699   -487
```

39l
```
 1  2140   2090
 2  4659   -456
 3  4654   -690
 4  1005  -1071
 5  1650   1585
```

3,10,l
```
 0  4555    435
 1  2049  -2287
 2  1681  -1703
```

3,10,l
```
 1  1492  -1571
 2  4561     81
 3  1163   1252
 4  4519    139
 5   894   -857
 6  2016   2163
```
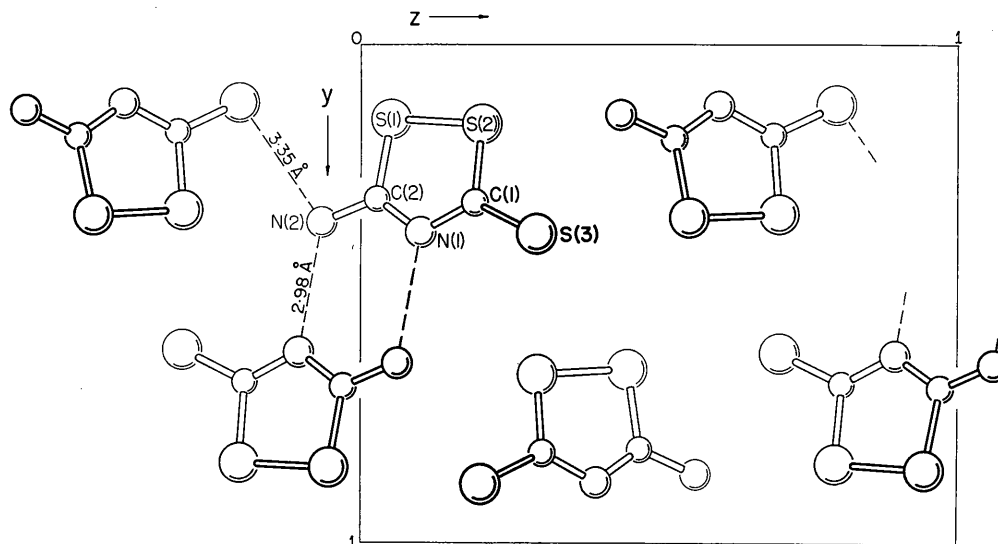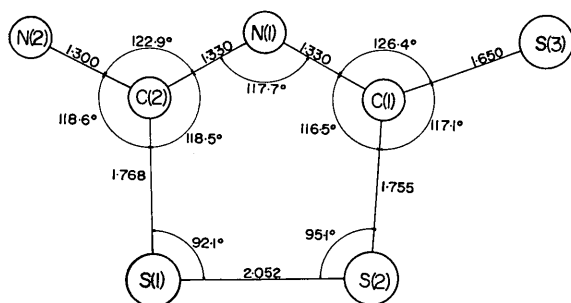
Fig. 4. The structure viewed along [100].

Fig. 5. Bond distances and angles for xanthane hydride.

Table 6. *Interatomic distances and angles*

Distances		Angles	
S(1)–S(2)	2·052 Å	S(1)–S(2)–C(1)	95·1°
S(1)–C(2)	1·768	S(2)–S(1)–C(2)	92·1
S(2)–C(1)	1·755	S(2)–C(1)–S(3)	117·1
S(3)–C(1)	1·650	S(2)–C(1)–N(1)	116·5
N(1)–C(1)	1·330	S(1)–C(2)–N(2)	118·6
N(1)–C(2)	1·330	S(1)–C(2)–N(1)	118·5
N(2)–C(2)	1·300	S(3)–C(1)–N(1)	126·4
		N(1)–C(2)–N(2)	122·9
		C(1)–N(1)–C(2)	117·7

Table 7. *Interatomic distances and angles involving hydrogen atoms*

Distances		Angles	
N(2)–H(1)	1·29 Å	C(2)–N(2)–H(1)	117°
N(2)–H(2)	1·28	C(2)–N(2)–H(2)	113
		H(1)–N(2)–H(2)	129

The equation for the least-squares plane through the molecule is

$$0.8890X - 0.2773Y - 0.3644Z' = 0.2238 \text{ Å},$$

where the direction cosines refer to the orthogonal axes abc^*. Deviations of the individual atoms for this plane are small but significant; they are:

S(1)	0·015 Å	N(1)	−0·002 Å
S(2)	−0·014	N(2)	−0·015
S(3)	0·005	C(1)	0·010
		C(2)	−0·010

The ring C–S bond lengths of 1·76 Å are only slightly shorter than the normal single-bond C–S distance of 1·81 Å, which indicates that the resonance stabilization is located mainly in the carbon and nitrogen part of the ring. The C–N(1) distances, 1·33 Å, are closely similar to those distances found in pyridine and other related resonating six-membered heterocyclics. The two major resonating forms, represented by formulae (I) and (II), seem to contribute equally to the structure, while other possibilities (III, IV, and V) appear to have only small (5 to 10%) contributions.

(I)

(II)

(III)

(IV)

(V)
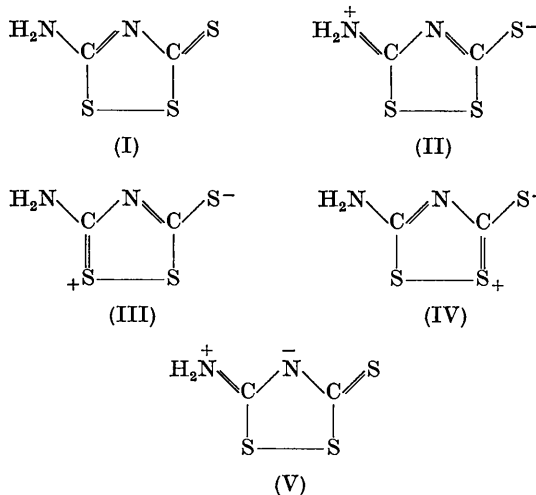
An interesting comparison can be made between xanthane hydride, thiuret hydrobromide (Foss & Tjomsland, 1958) and 4-methyl-1,2-dithia-4-cyclopentene-3-thione (Kehl & Jeffreys, 1958; Jeffreys & Shiono, 1959). The bond distances and angles found for these two structures are shown in Fig. 6. An analysis of the electronic structure of 1-2-dithia-4-cyclopentene-3-thione has been carried out by Bergson
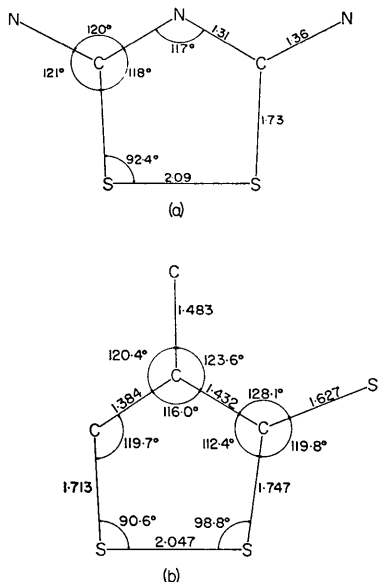
Fig. 6. Bond distances and angles for (a) thiuret ion and (b) 4-methyl-1,2-dithia-4-cyclopentene-3-thione.

(1962). It should be noted that the thiuret structure was solved only in projections, and that the thiuret ion contains a mirror plane perpendicular to the molecular plane. The standard deviations for the bond lengths in the thiuret ion are 0·012 Å for the S–S bond and 0·03 Å for the remainder; the standard deviations in the cyclopentenethione are 0·007 Å for the S–S bond, 0·017 Å for the S–C bonds, 0·024 Å for the ring C–C bonds, and 0·035 Å for the C–methyl-C bond. The distance reported for the non-ring C–N bond in the thiuret ion is slightly longer than that found in xanthane hydride. The S–S bond length in cyclopentenethione is in good agreement with that for xanthane hydride, but that for thiuret ion is somewhat longer. Within experimental error, agreement is found among the C–S single bonds in all three of the rings, the non-ring C–S bonds in cyclopentenethione and xanthane hydride, and the C–N bonds in the rings of xanthane hydride and the thiuret ion.

The intermolecular N · · · N and N · · · S distances seem reasonable for hydrogen bonding, and both hydrogen atoms are attached to N(2). The N(2)–H bond lengths are not significantly longer than the value normally expected. The packing of the molecules is quite tight with non-bonded sulfur–sulfur distances of 3·4 Å.

The difference map shown in Fig. 5 indicates peaks in approximately the correct places for the hydrogen atoms, but there are other peaks as well. The structure factors were recalculated with the anisotropic temperature factors readjusted in a manner suggested by the difference Fourier synthesis. In particular, the α for C(1) was raised to a value of 0·0460. For these calculations the R index was 0·072 and the sum of the weighted residuals increased by 10%. In a reflection-by-reflection examination of the observed and calculated structure factors, no trend was readily obvious, nor did any particular reflection show a distinct variation. In addition, the least-squares shifts for these calculations indicated no significant changes for the positional parameters and temperature factors except for C(1), whose α required a drastic reduction. Since this carbon atom is very close to the center of mass of the molecule, it may be expected to have a somewhat smaller temperature factor than the average, but the value obtained here seems too low. There are probably several sources for the additional peaks in the difference map and the anomalous temperature parameter: uncorrected absorption effects, the fact that data were collected around one axis only, the absence of data with $h > 3$, and the presence of the three sulfur atoms which contribute about 80% to the average intensity. It seems prudent, therefore, to treat the anisotropic temperature parameters with some scepticism.

References

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