

High-temperature X-ray studies indicate that cryolithionite is stable to about 660–680°C. Above this temperature an increasing disorder of the Na⁺ and the Li⁺ ions causes cryolithionite to become a part of the solid solution series (Na, Li)₃AlF₆, where the Na⁺ and Li⁺ ions are completely disordered. The mixed crystal of this composition melts at about 720°C. Note that the artificially formed cryolithionite probably contains some excess Li₃AlF₆, so that the formula should be written Na_{3-x}Li_{3+x}Al₂(LiF₄)₃. Preliminary studies indicate that *x* may be as large as 3/8.

Also lithium cryolite seems to undergo a similar order-disorder transition at temperatures above 700°C. This is indicated by a rapid change in the intensities of most of the cryolithionite reflections and the appearance of new reflections as the temperature is increased. By rapid cooling some of the disorder can be retained causing the observed lowering in the phase transition temperature as shown on Fig. 1b.

A preliminary study of the low-temperature modification of Li₃AlF₆ indicates that the compound has an orthorhombic structure with 8 units of LiAlF₆ in a cell of dimensions *a* = 8.39 Å, *b* = 11.92 Å, *c* = 7.82 Å. The calculated density is 2.748 g/cm³ as compared with the measured density 2.75 g/cm³. While the other alkali cryolites all have structures which are super structures of the perovskite structure (Wells ⁴), NaNa_{0.5}Al_{0.5}F₃—CaTiO₃, the present X-ray work indicates that lithium cryolite may have its structural analogues in the pyroxen group (ortho- and protoenstatite), Li_{0.5}Al_{0.5}LiF₃—Mg_{0.5}Mg_{0.5}SiO₃. According to this formula one third of the Li⁺ ions should be in 6-coordination while the other two thirds should be in 4-coordinated positions. If this assumption holds, the transformation to the cubic garnet structure should be associated with the following changes in coordination-number for the Li⁺ ions: One fourth of the Li⁺ ions in 4-coordination plus all the Li⁺ ions in 6-coordination should increase its coordination number to 8, while the rest remain in 4-coordination.

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Least Squares Refinement of the Molecular Structure of 1,2-Dithiolane-4-carboxylic Acid

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The crystal and molecular structure of 1,2-dithiolane-4-carboxylic acid, from two-dimensional *F_o—F_c* refinement of two zones, was reported by Foss and Tjomsland ¹ in 1958. The found S—S bond length and CSS/SSC dihedral angle were 2.096 ± 0.009 Å and 26.6 ± 1°, respectively.

One of us (A.H.) has recently shown that the sulphur-sulphur bond length in disulphides appears to vary with the dihedral angle, and that 2.10 Å probably is a better value than the generally accepted 2.08 Å for the length of a pure sulphur-sulphur single bond in a *cis* planar disulphide group.² Because the sulphur-sulphur bond length in 1,2-dithiolane-4-carboxylic acid played an important role in the considerations which led to that conclusion, a confirmation of the bond length, as found by the two-dimensional difference refinement, was sought. A least squares refinement of the structure has been undertaken with this view.

The crystals of 1,2-dithiolane-4-carboxylic acid are triclinic, with ¹*a* = 5.34 Å, *b* = 5.85 Å, *c* = 10.75 Å, α = 93½°, β = 89½°, γ = 109½°, and *Z* = 2. The space group is *C₂¹—P1*. In addition to the *0kl* and *h0l* reflections, on which the difference refinement ¹ was based, the least squares refinement comprises the reflec-

Table 1. Final atomic coordinates from the least squares refinement.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S ₁	0.6669	0.2263	0.1062
S ₂	0.8712	0.5910	0.1610
C ₃	0.6427	0.6181	0.2814
C ₄	0.4045	0.3805	0.2837
C ₅	0.3544	0.2543	0.1555
C ₆	0.4520	0.2200	0.3810
O ₁	0.6562	0.2731	0.4467
O ₂	0.2557	0.0159	0.3905
H ₁	0.730	0.667	0.374
H ₂	0.560	0.773	0.280
H ₃	0.207	0.063	0.166
H ₄	0.250	0.333	0.101
H ₅	0.223	0.417	0.321
H ₆	0.287	-0.100	0.460

tions of the diagonal zone $h\bar{h}l$, which were photographed and estimated during the earlier study, but not used there. Common reflections in $h0l$, $0kl$, and $h\bar{h}l$ were used to put all the reflections on the same scale. The least squares program used is designed by Mair,³ and weighting scheme No. 3, recommended by Mair, has been applied throughout the entire least squares process.

Refinement began with sulphur, oxygen, and carbon coordinates from the two-dimensional analysis.¹ Approximate hydrogen positions were obtained by projecting a wire-model of the molecule, with C-H = 1.1 Å and O-H = 1.0 Å, on to (010) and (100). Difference maps of the *a*- and *b*-axis projections, with all atoms but the hydrogens subtracted, have been reported earlier,¹ and the estimated hydrogen positions fall within positive areas of those maps. An overall isotropic temperature factor $\exp[-3(\sin^2\theta/\lambda^2)]$ was used as a start.

In the initial stages, the hydrogen parameters were fixed, and the non-hydrogen parameters and the scale factors were refined, first with isotropic temperature factors, and then with anisotropic temperature factors. Next both non-hydrogen and hydrogen parameters were refined, but the thermal parameters of the hydrogen atoms were kept fixed. Some low order reflections which were supposed to be affected by secondary extinction were given zero weight in the refinement. In the final structure factor calculation all unobserved reflections came out smaller than the corresponding threshold values. The final *R* index, excluding the reflections which were given zero weight is 7.6 %, based on 283 observed reflections.

Final atomic coordinates and temperature parameters are listed in Tables 1 and 2, and corresponding bond lengths and bond angles are given in Fig. 1.

The dihedral angle CSS/SSC in 1,2-dithiolane-4-carboxylic acid from the results of the present refinement, is $27.5 \pm 1^\circ$ and the length of the sulphur-sulphur bond is 2.096 ± 0.007 Å. Both values are in good agreement with those from the two-dimensional analysis.

C-S, C-C, and C-O bond lengths in 1,2-dithiolane-4-carboxylic acid, from the present refinement, may now be compared with expected values for the respective bonds. For C-S bonds a bond length of 1.82 Å has been proposed by Abrahams,⁴ and one arrives at the same value by adding the covalent radius of divalent sulphur, 1.05 Å,² to the *sp*³-radius of carbon, 0.77 Å. 1.82 Å is within one standard deviation of the C-S bond lengths, 1.803 and 1.808 ± 0.017 Å, given in Fig. 1.

The lengths of the cyclic C-C bonds, 1.51 and 1.54 ± 0.02 Å, agree within

Table 2. Final temperature parameters β_{ij} . The expression used is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{13})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
S ₁	0.0478	0.0411	0.0091	0.0153	-0.0024	0.0041
S ₂	0.0435	0.0388	0.0110	0.0096	0.0083	0.0087
C ₃	0.0741	0.0270	0.0088	0.0387	0.0110	0.0137
C ₄	0.0492	0.0322	0.0081	0.0196	0.0093	0.0076
C ₅	0.0337	0.0274	0.0089	0.0130	0.0026	-0.0084
C ₆	0.0429	0.0284	0.0067	-0.0473	0.0071	0.0057
O ₁	0.0486	0.0426	0.0106	-0.0192	0.0193	-0.0080
O ₂	0.0516	0.0342	0.0109	0.0015	0.0134	-0.0105

For the hydrogen atoms a temperature factor of $\exp[-4(\sin^2\theta/\lambda^2)]$ was used.

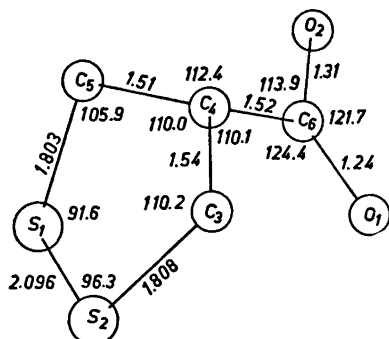


Fig. 1. Bond lengths (Å) and bond angles (°) in the 1,2-dithiolane-4-carboxylic acid molecule.

the limit of error with the length of a $C(sp^3)-C(sp^3)$ bond. Lide⁵ has proposed a bond length of 1.526 Å for such a bond, and Bastiansen and Trætterberg⁶ propose 1.534 Å. In a summary of $C(sp^3)-C(sp^3)$ bond lengths, Stoicheff⁷ lists values from 1.525 to 1.543 Å.

C_4-C_5 (Fig. 1) is a $C(sp^3)-C(sp^2)$ bond, and the found length, 1.52 ± 0.02 Å, agrees with the expected value, 1.504 Å,⁶ for this type of bond.

Surveys over bond lengths and angles in carboxyl groups have been reported by different authors.⁸⁻¹⁰ The C—OH and C=O bonds in Fig. 1, 1.31 and 1.24 ± 0.02 Å, respectively, agree with average values from these surveys. Thus the average C—OH and C=O bond-length for 28 different carboxyl groups, listed by Nardelli *et al.*,⁸ are 1.30 and 1.23 Å, respectively. Higgs and Sass⁹ arrive at a somewhat larger C—OH bond length, 1.35 Å, by averaging experimental values for formic, acetic, propionic, butyric, and valeric acid. The average value of C=O

bonds in the latter compounds is 1.24 Å. Higgs and Sass⁹ also give average values for the different bond angles in a carboxyl group. These values, $R-C-OH = 114^\circ$, $R-C=O = 124^\circ$, and $O=C-OH = 122^\circ$, are very close to the corresponding bond angles found in the present refinement, 113.9, 124.4, and $121.7 \pm 1^\circ$, respectively. In an accurate structure determination of salicylic acid,¹¹ the C—OH and C=O bond lengths of the carboxyl group were found to be 1.307 and 1.234 ± 0.005 Å, respectively, and the bond angles in the carboxyl group of salicylic acid, in the same order as above, were found to be 116.0, 122.9, and 121.2° , respectively.

Taking a difference of more than three times the standard deviation as real, it appears from Fig. 1 that the angle $C_4C_5S_1 = 105.9 \pm 1.0^\circ$ deviates significantly from the tetrahedral angle.

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