

## Bond-length/Dihedral-angle and Bond-length/Bond-order Relationships for Sulphur(II)-Sulphur(II) Bonds

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A literature survey indicates that in a disulphide group the normal dihedral angle of about  $90^\circ$  between the valencies of the two sulphur atoms, corresponds to S—S bond lengths of about 2.03 Å, while smaller dihedral angles give larger bond lengths. The difference in bond lengths is assumed to be partly due to lone pair repulsion which is most pronounced when the dihedral angle is  $0^\circ$ , and partly due to  $\pi$ -bonding which is most pronounced when the dihedral angle is  $90^\circ$ . A graph which shows this trend, indicates that 2.10 Å is the length of a single bond between two divalent sulphur atoms when the dihedral angle is  $0^\circ$ .

A linear bond-length/bond-order curve for sulphur-sulphur bonds in *cis* planar disulphide groups is proposed, based on the double-bond length 1.89 Å ( $S_2$ ) and the single bond length 2.10 Å. Calculated  $\pi$ -bond orders and experimental sulphur-sulphur bond lengths for 4-methyl-trithione and the 3- and 4-phenyl-1,2-dithiolium ions are in good agreement with the proposed bond-length/bond-order curve.

Structure studies of a series of compounds containing unsaturated five-membered disulphide rings have been undertaken by the author and co-workers.<sup>1-11</sup> The main purpose of these investigations has been to secure information for a better understanding of the conjugation in disulphide heterocycles. X-Ray crystallographic methods have been used, and so far the investigations comprise the molecular structures of xanthan hydride,<sup>1</sup> rhodan hydrate,<sup>2</sup> thiuret hydrobromide<sup>3</sup> and hydrochloride hemihydrate,<sup>4</sup> 3-phenyl-1,2-dithiolium iodide,<sup>5</sup> 4-phenyl-1,2-dithiolium iodide,<sup>6</sup> bromide,<sup>7</sup> and chloride monohydrate,<sup>7</sup> and 3,5-diacetamido-1,2-dithiolium bromide.<sup>8</sup> Furthermore, the sulphur-sulphur bond length in 3,5-diamino-1,2-dithiolium iodide has been determined,<sup>9</sup> and the structure of 3,5-diacetamido-1,2-dithiolium iodide<sup>10</sup> and 5-phenyl-3-(5-phenyl-1,2-dithiol-3-ylidenemethyl)-1,2-dithiolium iodide<sup>11</sup> have been worked out in one projection.

When the structure studies were initiated, the structures of two unsaturated five-membered cyclic disulphides had been reported in the literature: that of 4-methyl-trithione by Kehl and Jeffrey<sup>12</sup> in 1957, and that of thiuret hydroiodide by Foss and Tjomsland<sup>13</sup> in 1958. Jeffrey and Shiono<sup>14</sup> later refined the structure of 4-methyl-trithione by more advanced methods.

The sulphur-sulphur bond length in non-cyclic disulphides is normally found to be about 2.04 Å, and Jeffrey and Shiono<sup>14</sup> concludes that the sulphur-sulphur bond in 4-methyl-trithione, which is  $2.047 \pm 0.007$  Å, is a pure single bond. However, molecular orbital calculations carried out for 4-methyl-trithione by Bergson,<sup>15</sup> show that one should expect the sulphur-sulphur bond in this compound to be shortened by  $\pi$ -bonding; the calculated  $\pi$ -bond order for the sulphur-sulphur bond was 0.242. In thiuret hydroiodide the sulphur-sulphur bond length was found to be  $2.088 \pm 0.012$  Å, and thus appears to be significantly longer even than in non-cyclic disulphides. There seems to be no clear evidence as to whether sulphur(II)-sulphur(II) bonds of lengths 2.04–2.09 Å possess double-bond character or not; in the present paper an attempt is made to discuss this point on the basis of available information about bond lengths in relation to dihedral angles, with a view towards a subsequent evaluation of double-bond character of the sulphur-sulphur bond in unsaturated disulphides.

The most pronounced structural difference between a non-cyclic disulphide and an unsaturated cyclic five-membered disulphide, is that the disulphide group is non-planar in the former and planar in the latter. A dihedral angle of 90° between the planes of the valencies of the sulphur atoms in a disulphide group seems favourable, because the repulsion between lone-pair electrons on the two sulphur atoms has its minimum value associated with this configuration.<sup>16</sup> Thus the dihedral angles in non-cyclic disulphides and sulphur chains are usually found to be about 90°. Maximum lone-pair repulsion occurs when the dihedral angle is zero, *i.e.* in a *cis* planar disulphide group, and the stability of the planar disulphide group in unsaturated five-membered cyclic disulphides is then probably due to  $\pi$ -bonding in which  $\pi$ -orbitals on the sulphur atoms participate.<sup>13</sup>

One may thus suppose that the lone-pair repulsion energy in unsaturated five-membered cyclic disulphides is balanced by the energy gained by ring conjugation, and that this accounts for the stability of such a compound as contrasted with *saturated* five-membered cyclic disulphides. Of the latter type of compounds, the structure of 1,2-dithiolane-4-carboxylic acid has been reported;<sup>17</sup> the dihedral angle of the disulphide group is there  $27 \pm 1^\circ$  and the compound is unstable.

Sulphur-sulphur bond lengths between divalent sulphur atoms in non-cyclic compounds and in saturated cyclic compounds are listed in Table 1 and shown in Fig. 1. The survey comprises sulphur(II)-sulphur(II) bond lengths for which the accuracy is  $\pm 0.02$  Å or better, and for which the dihedral angle of the planes of the valencies are known. Fig. 1 shows that if the Pauling value 2.08 Å is taken as the length of a pure single bond between divalent sulphur atoms, one would probably ascribe some double bond character to most any bond in Fig. 1.

It has been shown that if an average is taken of a large number of sulphur-sulphur bond lengths,<sup>18</sup> neglecting the valence state of the sulphur-sulphur atoms involved, one arrives at a value close to 2.08 Å which by chance seems to be close to a relevant bond length for a pure single bond between two divalent sulphur atoms.

One gets the idea from Fig. 1 that the sulphur-sulphur bond length between two divalent sulphur atoms varies with the dihedral angle. The smallest

Table 1. Sulphur(II)-sulphur(II) bond lengths and corresponding dihedral angles in different compounds.

Compound	S-S (Å)	-SS/SS- (°)	Ref.
1,2-Dithiolane-4-carboxylic acid	2.096 ± 0.007	27 ± 1	17, 19
Sporidesmin	2.096* ± 0.02	8.5 ± 3	20
1,2-Dithiane-3,6-dicarboxylic acid	2.069 ± 0.015	60.3 ± 2	21
Rhombohedral sulphur S <sub>6</sub>	2.057 ± 0.018	74.5 ± 2.5	22
Orthorhombic sulphur S <sub>8</sub>	2.048 ± 0.002	98.7 ± 0.5	23
» » »	2.047 **		24
L-Cystine dihydrochloride	2.044 ± 0.01	79.2 ± 2	25
N,N'-Diglycyl-L-cystine dihydrate	2.04 ± 0.005	101 ± 2	26
Formamidinium disulphide diiodide monohydrate	2.044 ± 0.02	104.8 ± 3	27
Formamidinium disulphide dibromide monohydrate	2.044 ± 0.01	89.2 ± 2	27
Potassium barium hexathionate	2.05 ± 0.02	108 ± 2	28
	2.04 ± 0.02	105 ± 2	
	2.04 ± 0.02	89 ± 2	
The pentathionate ion in barium salts	2.04 ± 0.02	108 ± 1.5	29
<i>trans</i> -Dichlorobis(ethylenediamine)-cobalt(III) hexathionate monohydrate	2.054 ± 0.010	73.2 ± 1.5	30
	2.025 ± 0.015	85.2 ± 1.5	
Perchlorodimethyltrisulphide	2.037 ± 0.010	95 ± 2	31
	2.032 ± 0.010	93 ± 3	
Diphosphorus hexathiodibromide	2.034 ± 0.015	86 ± 1.2	32
L-Cystine	2.032 ± 0.004	74 ± 1	33
L-Cystine dihydrobromide	2.024 ± 0.014	90 ± 2	34
Sodium tetrathionate dihydrate	2.019 ± 0.010	90.4 ± 1	35
Tetramethylthiuram disulphide	2.00 ± 0.01	88 ± 2	36

\* This bond length and the dihedral angle have been calculated by the author from the reported coordinates in Ref. 20. The standard deviations are rough estimates.

\*\* Value without correction for rigid-body libration.

bond lengths seem to correspond to dihedral angles of about 90°, while the largest bond lengths apparently correspond to small dihedral angles. In order to expose this trend more clearly, bonds with dihedral angle between 70 and 110° were divided into five groups, 70–80°, 80–88°, 88–92°, 92–100°, and 100–110°, and the average bond length for each group were calculated. The bond lengths were given weights inversely proportional to their respective standard deviations, and in cases where the dihedral angle, by adding or subtracting its standard deviation, entered a neighbouring group, the corresponding bond length was counted there too. The result is shown in Fig. 2, where a curve is tentatively drawn through the "average" points and the points which represent the sulphur-sulphur bond length and corresponding dihedral angles for 1,2-dithiane-3,6-dicarboxylic acid,<sup>21</sup> 1,2-dithiolane-4-carboxylic acid,<sup>13,19</sup> and sporidesmin.<sup>20</sup>

According to Fig. 2 the sulphur-sulphur bond is about 0.07 Å longer in a *cis* planar disulphide group than in a disulphide group with dihedral angle 90°.

Bergson<sup>37</sup> has derived expressions which give the energy barrier to internal rotation around the sulphur-sulphur bond. From these expressions he finds that *p*-orbital repulsion causes a torsion barrier of 13.8–15.7 kcal/mole and

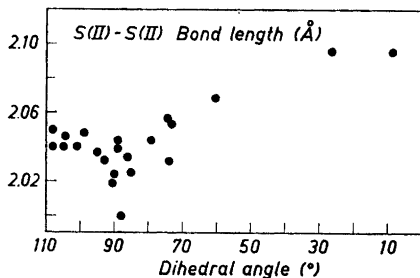


Fig. 1. A representation of the bond-length and corresponding dihedral angles given in Table 1.

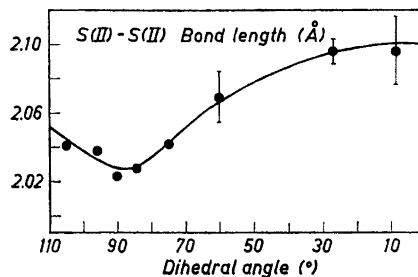


Fig. 2. The variation of sulphur(II)-sulphur(II) bond length with dihedral angle.

$sp^3$ -orbital repulsion causes a torsion barrier of 6.2–7.0 kcal/mole. From the torsional frequencies of the sulphur-sulphur bond as observed in Raman spectra, barrier heights of 9.5, 13.2 and 14.2 kcal/mole for dimethyl disulphide, diethyl disulphide and disulphur dichloride have been deduced, and from calculated and observed entropy and heat capacity, an effective barrier height of 6.8 kcal/mole for dimethyl disulphide, *cf.* Ref. 38.

Huggins<sup>39</sup> and Davis *et al.*<sup>40</sup> have discussed expressions which correlate bond energy and bond length. According to Huggins a sulphur-sulphur bond difference of 0.07 Å (2.10–2.03 Å) would correspond to a difference in bond energy of about 16 kcal/mole; according to Davis *et al.* the difference would be about 6 kcal/mole. When these figures are compared with those calculated by Bergson for the torsion barrier, it becomes evident that the indicated variation in sulphur-sulphur bond length with dihedral angle, at least to some extent reflects lone-pair repulsion. It is difficult to decide whether the lone-pair repulsion alone accounts for the indicated bond difference of 0.07 Å and for the barrier height, because of the rather poor agreement of the bond energy differences.

It seems likely that the shortening of the sulphur-sulphur bond for dihedral angles of 90°, and the prevalence of this dihedral angle, may to some extent, *cf.* Ref. 41, be caused also by  $\pi$ -bonding arising from overlap of the  $p$   $\pi$ -electron pair of one divalent sulphur atom with 3*d*-orbitals of a bond partner. Results from structure investigations of disulphur dihalides<sup>42,43</sup> may be taken to indicate that such bonding generally should be considered in connection with disulphides when the dihedral angle is about 90°.

The structure of disulphur difluoride, S<sub>2</sub>F<sub>2</sub>, has been determined by microwave methods;<sup>42</sup> the dihedral angle FSS/SSF is 87.9 ± 1.5° and the sulphur-sulphur bond length is 1.888 ± 0.01 Å. Disulphur dichloride and dibromide have been investigated by electron diffraction;<sup>43</sup> the dihedral angle XSS/SSX and sulphur-sulphur bond length are 82.5 ± 12° and 1.97 ± 0.03 Å in the former and 83.5 ± 11° and 1.98 ± 0.04 Å in the latter.

One of the different explanations<sup>42</sup> proposed for the rather unusual sulphur-sulphur bond length in S<sub>2</sub>F<sub>2</sub> is a bonding pattern with  $\pi$ -bonding arising from  $p$ - $d$  overlap as that mentioned above. The sulphur 3*d* orbitals contract due to the electronegative fluorine substituent,<sup>44</sup> and pronounced  $\pi$ -bonding

is established through efficient  $p-d$  overlap. At  $90^\circ$  dihedral angle, two  $p-d$   $\pi$ -overlaps, at right angles, per S-S bond would be possible. Since chlorine and bromine are less electronegative than fluorine, there will be less contraction of sulphur  $3d$  orbitals in  $S_2Cl_2$  and  $S_2Br_2$  than in  $S_2F_2$ , therefore less efficient  $p-d$  overlap and longer sulphur-sulphur bonds. This agrees with the experimental results cited above, and thinking along this line, it seems probable that in a disulphide with dihedral angle about  $90^\circ$  there may be some  $\pi$ -bonding in the sulphur-sulphur bond also when the atoms bonded to sulphur are, say, sulphur or carbon.

Fehér and Münzner<sup>45</sup> have studied the UV spectra of compounds containing sulphur chains and suggested that  $\pi$ -bonding probably occurs along the chain. Measurements of diamagnetic susceptibility, undertaken by Fava and Ilicito<sup>46</sup> on compounds containing sulphur chains, were interpreted as indicating partial double-bond character of the sulphur-sulphur bonds. Foss and Tjomsland<sup>29</sup> assume that the middle sulphur-sulphur bonds in the pentathionate ion possess some double-bond character. The following sulphur-sulphur bond lengths have been reported for cesium hexasulphide by Abrahams and Grison:<sup>47</sup>  $S_1-S_2 = 1.99 \text{ \AA}$ ,  $S_2-S_3 = 2.10 \text{ \AA}$ ,  $S_3-S_4 = 2.03 \text{ \AA}$ ,  $S_4-S_5 = 2.12 \text{ \AA}$ , and  $S_5-S_6 = 2.03 \text{ \AA}$ , and the dihedral angles:  $S_1S_2S_3/S_2S_3S_4 = 78^\circ 46'$ ,  $S_2S_3S_4/S_3S_4S_5 = 81^\circ 56'$  and  $S_3S_4S_5/S_4S_5S_6 = 61^\circ 24'$ . The authors<sup>47</sup> suggest that the sulphur-sulphur bonds of length  $2.02 \text{ \AA}$  in the hexasulphide ion each possess one-third double bond character; the two extra electrons in the hexasulphide ion are assumed to be localized in the three shorter sulphur-sulphur bonds.

The latter suggestion by Abrahams and Grison implies that two of the sulphur-sulphur bonds in the hexasulphide chain, found to be  $2.12$  and  $2.10 \pm 0.03 \text{ \AA}$ , respectively, are pure  $\sigma$ -bonds. This, however, does not quite agree with the trend of Fig. 2. If the curve in Fig. 2 is used for predicting bond lengths in the hexasulphide ion on the basis of the dihedral angles found by Abrahams and Grison,<sup>47</sup> one finds that their longest sulphur-sulphur bond ( $2.12 \text{ \AA}$ ) should be  $2.07 \text{ \AA}$  and the two other central sulphur-sulphur bonds, found to be  $2.10$  and  $2.03 \text{ \AA}$ , respectively, should be  $2.04$  and  $2.03 \text{ \AA}$ , respectively. The alternating variation in bond length along the sulphur chain in the hexasulphide ion, found by Abrahams and Grison,<sup>47</sup> disagrees with the author's interpretation of Fig. 2. However, a least squares refinement of the molecular structure of cesium hexasulphide has been carried out by Sletten and the author,<sup>48</sup> on the structure factor data published by Abrahams and Grison.<sup>47</sup> The three central sulphur-sulphur bond lengths in the hexasulphide ion which Abrahams and Grison report to be  $2.10$ ,  $2.03$ , and  $2.12 \pm 0.03 \text{ \AA}$ , and which according to the dihedral angles and Fig. 2 should be  $2.04$ ,  $2.03$ , and  $2.07 \text{ \AA}$ , were from the mentioned least squares refinement found to be  $2.04$ ,  $2.02$ , and  $2.11 \pm 0.03 \text{ \AA}$ , respectively.

The average length of terminal sulphur-sulphur bonds in barium tetrasulphide monohydrate<sup>49</sup> and cesium hexasulphide<sup>47</sup> is  $2.02 \text{ \AA}$ . If the two extra electrons in polysulphide ions are localized on the end sulphurs, which seems reasonable to believe, these sulphur atoms will be electronically equivalent to chlorine atoms in the same positions. One may assume that the end sulphurs in polysulphide ions will arrange themselves in such a way as to

obtain minimum lone-pair repulsion and maximum  $\pi$ -overlap if the environment allows it. It therefore seems quite logical that the length of the terminal bonds should be found to be about 2.02 Å. The two central sulphur-sulphur bonds in the tetrasulphide ion, both  $2.07 \pm 0.04$  Å, deviate by less than a standard deviation from the value 2.045 which may be predicted from the dihedral angle and Fig. 2.

Fig. 2 indicates a sulphur-sulphur single bond length of about 2.03 Å at  $90^\circ$  dihedral angle, if lone-pair repulsion alone accounts for the variation of sulphur-sulphur bond length with dihedral angle. The covalent radius of divalent sulphur would then be 1.01–1.02 Å, in which case the concept of additive covalent radii would work rather poorly in predicting bond lengths between divalent sulphur and other atoms. As a matter of fact a covalent radius for divalent sulphur of 1.05 Å gives according to experience better fits. This indicates that both lone-pair repulsion and  $\pi$ -bonding accounts for the observed sulphur-sulphur bond length differences. Which of these effects is predominant can hardly be decided at present.

Fortunately, one needs not consider what causes the variation of sulphur-sulphur bond length with dihedral angle when trying to find a relevant value for the sulphur-sulphur single-bond length in a *cis* planar disulphide group. It seems clear from Fig. 2 that this value may be taken as 2.10 Å. However, the bond lengths which the curve in Fig. 2 is based on are not corrected for rigid-body libration, and may have to be adjusted slightly upwards when more sulphur-sulphur bond lengths for which rigid-body corrections have been undertaken, become available.

A linear bond-length/bond-order graph is suggested, as shown in Fig. 3. The length of the sulphur-sulphur bond is there put equal to that found in  $S_2$ , 1.89 Å,<sup>18</sup> and the single-bond length is taken as 2.10 Å according to the present paper. The graph is meant as a guide for estimating the double bond character of sulphur-sulphur bonds in *cis* planar disulphide groups from bond length values. Some other bond-length/bond-order relations are indicated on the graph. These are for 4-methyl-trithione<sup>14,15</sup> ( $S-S = 2.047 \pm 0.007$  Å and  $\pi$ -order = 0.242), the 3-phenyl-1,2-dithiolium ion<sup>5</sup> ( $S-S = 2.00 \pm 0.01$  Å and  $\pi$ -order = 0.426) and the 4-phenyl-1,2-dithiolium ion<sup>6,7</sup> ( $S-S = 2.015 \pm 0.010$  Å and  $\pi$ -order = 0.405). The bond orders for the 3- and 4-phenyl-substituted 1,2-dithiolium ions have been calculated by Sletten and the author according to a self-consistent parameter M.O. method by Bergson.<sup>15</sup> It may be added that excitation energies from calculated M.O. energy levels of the phenyl-substituted 1,2-dithiolium ions, are in good agreement with reported UV spectra<sup>50</sup> for the compounds. This will be discussed in a later paper.<sup>51</sup>

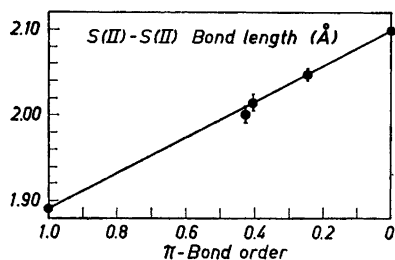


Fig. 3. Proposed bond-length/bond-order curve for sulphur(II)-sulphur(II) bonds.

*Acknowledgement.* The author wishes to express his sincere thanks to Professor Olav Foss for encouragement and for many helpful discussions.

## REFERENCES

1. Hordvik, A. *Acta Chem. Scand.* **15** (1961) 1186; **17** (1963) 2575.
2. Hordvik, A. *Acta Chem. Scand.* **14** (1960) 1218; **20** (1966) 754.
3. Hordvik, A. and Joys, S. *Acta Chem. Scand.* **19** (1965) 1539.
4. Hordvik, A. and Sletten (Sundsford), J. *Acta Chem. Scand.* **19** (1965) 753; **20** (1966) 1907.
5. Hordvik, A. and Kjøge, H. M. *Acta Chem. Scand.* **19** (1965) 935.
6. Hordvik, A. and Sletten, E. *Acta Chem. Scand.* **20** (1966) 1874.
7. Grundtvig, F., Hordvik, A. and Baxter, R. M. *To be published.*
8. Hordvik, A. and Kjøge, H. M. *Acta Chem. Scand.* **20** (1966) 1923.
9. Hordvik, A. *Acta Chem. Scand.* **19** (1965) 1039.
10. Hordvik, A. and Kjøge, H. M. *Acta Chem. Scand.* **19** (1965) 523.
11. Hordvik, A. *Acta Chem. Scand.* **19** (1965) 1253.
12. Kehl, W. L. and Jeffrey, G. A. *Acta Cryst.* **10** (1957) 807; **11** (1958) 813.
13. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1799.
14. Jeffrey, G. A. and Shiono, R. *Acta Cryst.* **12** (1959) 447.
15. Bergson, G. *Arkiv Kemi* **19** (1962) 181.
16. Bergson, G. *Arkiv Kemi* **12** (1957) 233.
17. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 1810.
18. Abrahams, S. C. *Quart. Rev. (London)* **10** (1956) 407.
19. Foss, O., Hordvik, A. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 1169.
20. Fredrichsons, J. and Mathieson, A. McL. *Acta Cryst.* **18** (1965) 1043.
21. Foss, O., Johnsen, K. and Reistad, T. *Acta Chem. Scand.* **18** (1964) 2345.
22. Donohue, J., Caron, A. and Goldish, E. *J. Am. Chem. Soc.* **83** (1961) 3748.
23. Cooper, A. S., Bond, W. L. and Abrahams, S. C. *Acta Cryst.* **14** (1961) 1008.
24. Caron, A. and Donohue, J. *Acta Cryst.* **18** (1965) 562.
25. Steinrauf, L. K., Peterson, J. and Jensen, L. H. *J. Am. Chem. Soc.* **80** (1958) 3835.
26. Yakel, H. L., Jr. and Hughes, E. W. *Acta Cryst.* **7** (1954) 291.
27. Foss, O., Johnsen, J. and Tvedten, O. *Acta Chem. Scand.* **12** (1958) 1782.
28. Foss, O. and Johnsen, K. *Acta Chem. Scand.* **19** (1965) 2207.
29. Foss, O. and Tjomsland, O. *Acta Chem. Scand.* **12** (1958) 44.
30. Foss, O. and Marøy, K. *Acta Chem. Scand.* **19** (1965) 2219.
31. Berthold, H. J. *Z. Krist.* **116** (1961) 290.
32. Einstein, F. W. B., Penfold, B. R. and Tapsell, Q. T. *Inorg. Chem.* **4** (1965) 186.
33. Oughton, B. M. and Harrison, P. M. *Acta Cryst.* **12** (1959) 396.
34. Peterson, J., Steinrauf, L. K. and Jensen, L. H. *Acta Cryst.* **13** (1960) 104.
35. Foss, O. and Hordvik, A. *Acta Chem. Scand.* **18** (1964) 662.
36. Marøy, K. *Acta Chem. Scand.* **19** (1965) 1509.
37. Bergson, G. *Some New Aspects of Organic Disulphides, Diselenides and Related Compounds*, Abstracts of Uppsala Dissertations in Science **13** (1962).
38. Foss, O. *Advan. Inorg. Chem. Radiochem.* **2** (1960) 237, p. 268.
39. Huggins, M. L. *J. Am. Chem. Soc.* **75** (1953) 4126.
40. Davis, R. E., Louis, B. L. and Cohen, A. *J. Am. Chem. Soc.* **88** (1966) 1.
41. Krebs, H. Z. *Naturforsch.* **12b** (1957) 795, p. 800.
42. Kuczowski, R. L. *J. Am. Chem. Soc.* **86** (1964) 3617.
43. Hirota, E. *Bull. Chem. Soc. Japan* **31** (1958) 130.
44. Sutton, L. E. *Chemische Bindung und Molekülstruktur*, Springer, Berlin 1961.
45. Fehér, F. and Münzner, H. *Chem. Ber.* **96** (1963) 1131.
46. Fava, A. and Ilicito, A. *Ann. Chim. (Rome)* **43** (1953) 509.
47. Abrahams, S. C. and Grison, E. *Acta Cryst.* **6** (1953) 206.
48. Hordvik, A. and Sletten, E. *Acta Chem. Scand.* *To be published.*
49. Abrahams, S. C. *Acta Cryst.* **7** (1954) 423.
50. Klingsberg, E. *J. Am. Chem. Soc.* **83** (1961) 2934.
51. Hordvik, A. and Sletten, E. *Acta Chem. Scand.* **20** (1966) 1938.

Received March 26, 1966.