

The  $\beta$ -ketoamine coordinates through O, and the U atom exhibits pentagonal-bipyramidal coordination. In our previous determination (Haigh, Nassimbeni, Paup-tit, Rodgers & Sheldrick, 1976), intramolecular hydrogen bonding between the amino H and keto O atoms causes the  $\beta$ -ketoamine to adopt a ring-like structure and to display pseudo-aromaticity, as evidenced by the ligand's planarity. In the present complex, which is di-substituted at N, the  $\beta$ -ketoamine adopts an open chain structure which is not planar (plane 4, Table 5). As expected, the intersection angle ( $48^\circ$ ) of the  $\beta$ -ketoamine and the plane through the five equatorial O atoms is larger than that observed in part I, where a second hydrogen bond between the amino H and an acetylacetonate O atom holds the ligand plane at  $32^\circ$  to the equatorial plane.

Fig. 2 is a view of the complex along the bisector of

the O(3)—U—O(6) angle with the H atoms omitted for clarity. Each acetylacetonate ring is slightly folded about an axis through its O atoms making angles of  $6.0$  and  $5.0^\circ$ .

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#### References

- HAIGH, J. M., NASSIMBENI, L. R., PAUP-TIT, R. A., RODGERS, A. L. & SHELDRIK, G. M. (1976). *Acta Cryst.* B32, 1398–1401.  
 HAIGH, J. M. & THORNTON, D. A. (1971). *J. Inorg. Nucl. Chem.* 33, 1787–1797.  
 SHELDRIK, G. M. (1977). To be published.

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### The Stereochemistry of Disulfides. The Crystal Structure of $1\alpha,5\alpha$ -Epidithioandrostane- $3\alpha,17\beta$ -diol ( $C_{19}O_2S_2H_{30}$ )

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Crystals of the title compound (I) are monoclinic, space group  $P2_1$ . Unit-cell constants [ $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ ,  $t = -160 \pm 5^\circ\text{C}$ ] are  $a = 12.480$  (14),  $b = 7.210$  (9),  $c = 20.978$  (24)  $\text{\AA}$ ;  $Z = 4$  with two crystallographically independent molecules [(Ia) and (Ib)]. A final set of 3495 unique intensities, of which 3459 were non-zero, was obtained by averaging redundancies in the 7011 reflections collected by diffractometry. The structure was solved by direct methods and refined by full-matrix least squares to  $R(F) = 0.044$  and  $R_w(F) = 0.037$ . The C—S—S—C torsion angles are  $-2.5$  and  $-4.5^\circ$ , with S—S bond distances of  $2.104$  (2) and  $2.101$  (2)  $\text{\AA}$ , for (Ia) and (Ib). Geometries of 18 molecules containing C—S—S—C fragments are compared and the conformations of 1,2-dithiolane rings are discussed. Large conformational differences are observed in the D rings of (Ia) and (Ib). Comparisons of the structures of (I) and  $5\alpha$ -androstane- $3\alpha,17\beta$ -diol (II) [Precigoux, Busetta, Courseille & Hospital, *Cryst. Struct. Commun.* (1972), 1, 265–268] show the distortions of the androstane skeleton necessary to accommodate the 1,5-diaxial disulfide. Short intramolecular O—H...S contact distances of  $2.50$  to  $2.65 \text{ \AA}$  are observed. The molecules form continuous intermolecular hydrogen-bonded chains arranged in a left-handed helix parallel to the  $b$  axis.

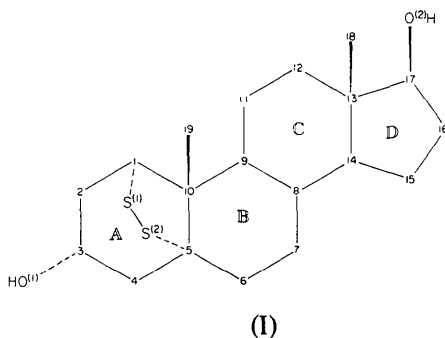
#### Introduction

$1\alpha,5\alpha$ -Epidithioandrostane- $3\alpha,17\beta$ -diol (I) is of current interest as a model compound for correlations of the chiroptical properties and stereochemistry of disulfides (Neubert & Carmack, 1974). The structure determination of (I) has been undertaken to (1) confirm the

proposed structure (Tweit & Dodson, 1959; Harpp & Gleason, 1970); (2) establish the disulfide dihedral angle which has been previously estimated, from model studies and from the wavelength of the lowest-energy electronic transition (Bergson, Sjöberg, Tweit & Dodson, 1960), to be close to  $0^\circ$ ; and (3) establish the environment about the disulfide chromophore. Comparisons of the structures of (I) and  $5\alpha$ -androstane- $3\alpha,17\beta$ -diol (II) (Precigoux, Busetta, Courseille & Hospital, 1972) have been undertaken to show the

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molecular distortion resulting from the replacement of the 1-axial and 5-axial H atoms in (II) with a 1,5-diaxial disulfide.



### Experimental

A sample of (I) ( $C_{19}O_2S_2H_{30}$ ), kindly provided by G. D. Searle & Co., was recrystallized from methanol by slow evaporation of solvent at ambient temperature producing yellow (long-wavelength tail of the 370 nm electronic transition), transparent needles. A well formed crystal of dimensions  $0.31 \times 0.35 \times 0.40$  mm was mounted on a glass fiber by means of silicone grease and placed on the diffractometer using an ultra-stable goniometer of our own design which features translations only. The crystal was then cooled to  $-160 \pm 5^\circ\text{C}$  with a gas-flow cooling system (Huffman, 1974).

A systematic search of a limited hemisphere (Huffman, 1974) revealed a monoclinic cell with systematic extinctions of  $k$  odd for  $0k0$ . Cell parameters were determined by a least-squares fit of 14 reflections centered in  $\pm 2\theta$ . Crystal data are given in Table 1. The diffractometer used was a Picker FACS-1 equipped with a highly oriented graphite monochromator (002 reflection), with Mo radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Data were collected at  $-160^\circ\text{C}$  with a standard  $\theta$ - $2\theta$  scan technique and fixed  $\theta$ - $2\theta$  backgrounds. A scan speed of  $2^\circ \text{ min}^{-1}$  over the range  $K\alpha_1 - 1^\circ$  to  $K\alpha_2 + 1^\circ$  with 10 s background counts was used and no attenuators were necessary. 7011 reflections (including redundancies) were collected for  $\pm h + k \pm l$  for  $1^\circ < 2\theta < 50^\circ$ . Three reflections,

Table 1. *Crystal data*

$C_{19}O_2S_2H_{30}$ , $M_r = 354.56$	
Space group $P2_1$	
Systematic extinctions: $k$ odd for $0k0$	
$a = 12.480 (14) \text{ \AA}$	$D_{\text{calc}} = 1.301 \text{ g cm}^{-3}$
$b = 7.210 (9)$	$D_{\text{obs}} (\text{floatation}) = 1.28 (1)$
$c = 20.978 (24)$	$\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$
$\beta = 106.44 (6)^\circ$	$\mu = 2.89 \text{ cm}^{-1}$
$V = 1810.46 \text{ \AA}^3$	$t = -160 \pm 5^\circ\text{C}$
$Z = 4$	

chosen as standards, were monitored after every 50 measurements and indicated no systematic trends. Diffractometer constants and data-reduction formulae are given elsewhere (Visscher, Huffman & Streib, 1974). The ignorance factor was chosen to be 0.02 based on prior experience, and the redundant data were averaged to yield a final set of 3495 unique intensities, of which 3459 were non-zero.

### Solution and refinement

The data were converted to normalized structure factors ( $E$ ) and the phases of the latter were determined by direct methods (Germain, Main & Woolfson, 1971). An  $E$  map based on these phases located the four S atoms and 12 of the C atoms. Two successive Fourier syntheses were required to locate the remaining non-hydrogen atoms. Isotropic refinement at this stage converged rapidly to  $R(F) = 0.120$  and  $R_w(F) = 0.113$ , where  $R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$  and  $R_w(F) = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}}{\sum w(|F_o| - |F_c|)^2}$ , where  $w = 1/\sigma(F_o)^2$ . A difference Fourier synthesis located all but six of the H atoms, with electron densities of  $0.35$  to  $0.92 \text{ e \AA}^{-3}$ . The remaining six H atoms were placed in calculated positions and all non-hydrogens were then refined anisotropically. Scattering factors and anomalous dispersion terms for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), and the values for the H scattering factors were taken from the tabulation of Stewart, Davidson & Simpson (1965).

In the final cycles all atoms were refined, with anisotropic thermal parameters for the non-hydrogen atoms and isotropic parameters for the H atoms. It was necessary to refine the two crystallographically independent molecules separately because of computer limitations. The final residuals were  $R(F) = 0.044$  and  $R_w(F) = 0.037$ , and the goodness-of-fit for the last cycle was 1.11, with the largest  $\Delta/\sigma$  being 0.02. No extinction correction was necessary, and no absorption corrections were performed [estimated maximum and minimum transmission coefficients are 82.4 and 86.1% for  $\mu(\text{Mo } K\alpha) = 2.888 \text{ cm}^{-1}$ ]. A final difference Fourier synthesis was essentially featureless, with one relatively large peak of  $0.82 \text{ e \AA}^{-3}$  lying near S(1), and all other peaks of less than  $0.35 \text{ e \AA}^{-3}$ .

Final positional and thermal parameters are given in Tables 2 and 3.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32142 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England. Tables are also available, in microfiche form only, for \$2.50 from the Chemistry Library, Indiana University, Bloomington, Indiana 47401, USA. Specify Molecular Structure Center Report No. 7517.

## Discussion

Bond lengths and bond angles for the two crystallographically independent molecules (Ia) and (Ib) are given in Tables 4 and 5. For equivalent bond lengths, the mean value of  $|d_a - d_b|/(\sigma_a^2 + \sigma_b^2)^{1/2}$  is 1.1; for equivalent bond angles the corresponding value is 1.4. Bond lengths and angles with  $|d_a - d_b|/(\sigma_a^2 + \sigma_b^2)^{1/2} > 2.0$  are indicated in the tables. The relatively small thermal ellipsoids and overall precision obtained is typical of low-temperature crystallographic results. The

average C—H bond distance is 0.953, with individual distances varying from 0.844 to 1.020 Å. The average H—C—H angle is 105.1°.

The unit-cell packing, with hydrogen bonds indicated, is shown in Fig. 1, and a stereo view of molecule (Ia) is given in Fig. 2. In both molecules, H(O1) participates in intramolecular hydrogen bonding to one or both S atoms (see below), leaving only the 17 $\beta$ -hydroxyls [H(O2)] to act as proton donors in intermolecular hydrogen bonding. The difference between the two molecules results from the different

Table 2. Fractional coordinates and anisotropic thermal parameters (all  $\times 10^5$ ) for non-hydrogen atoms

Primed atoms refer to molecule Ib. The form of the exponent is:  $-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hbl_{13} + 2klb_{23})$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> <sub>11</sub>	<i>b</i> <sub>22</sub>	<i>b</i> <sub>33</sub>	<i>b</i> <sub>12</sub>	<i>b</i> <sub>13</sub>	<i>b</i> <sub>23</sub>
S(1)	5976 (7)	-24391*	7235 (4)	244 (6)	892 (19)	126 (2)	68 (9)	83 (3)	13 (6)
S(2)	1359 (7)	-2075 (15)	12360 (4)	200 (6)	744 (19)	118 (2)	-73 (9)	42 (3)	-44 (6)
C(1)	94876 (27)	59976 (53)	8498 (16)	241 (23)	731 (71)	78 (8)	18 (35)	26 (11)	-48 (21)
C(2)	-974 (27)	-51097 (55)	14934 (17)	253 (23)	637 (74)	124 (9)	-42 (37)	41 (12)	-63 (24)
C(3)	1517 (29)	60433 (57)	21355 (17)	312 (25)	974 (80)	80 (9)	57 (38)	2 (12)	8 (22)
C(4)	-6856 (28)	-23502 (58)	20864 (16)	315 (24)	906 (75)	77 (8)	-59 (40)	44 (11)	-76 (24)
C(5)	-10897 (26)	-13728 (52)	14114 (16)	156 (21)	673 (70)	81 (8)	-58 (34)	39 (11)	-17 (21)
C(6)	-19491 (27)	1347 (52)	14301 (16)	263 (24)	825 (78)	65 (8)	-59 (36)	17 (11)	-81 (21)
C(7)	-24768 (28)	10536 (51)	7595 (17)	275 (25)	550 (68)	92 (9)	-0 (34)	45 (12)	-32 (21)
C(8)	70666 (25)	96688 (53)	2002 (15)	176 (21)	586 (67)	79 (8)	-37 (35)	39 (10)	-16 (23)
C(9)	-20142 (26)	-17387 (53)	1646 (16)	157 (21)	803 (71)	76 (8)	-18 (34)	44 (11)	-6 (21)
C(10)	-15446 (26)	-27757 (50)	8369 (16)	211 (22)	601 (74)	82 (8)	-85 (33)	46 (11)	-60 (21)
C(11)	-23849 (28)	-30301 (53)	-4427 (17)	348 (25)	598 (73)	97 (9)	60 (36)	57 (12)	-43 (22)
C(12)	-28537 (27)	-19761 (55)	-10973 (16)	234 (23)	1040 (83)	83 (9)	7 (36)	45 (11)	-74 (22)
C(13)	61988 (26)	93231 (51)	89367 (16)	200 (22)	717 (73)	75 (8)	-62 (35)	20 (11)	-46 (21)
C(14)	66509 (27)	6553 (52)	95306 (16)	167 (22)	755 (74)	87 (8)	-23 (34)	37 (11)	-35 (22)
C(15)	-42517 (28)	21370 (53)	-5677 (17)	288 (25)	733 (79)	97 (9)	-21 (35)	25 (11)	-33 (21)
C(16)	-46283 (29)	24164 (59)	-13268 (17)	322 (25)	921 (78)	100 (9)	145 (40)	17 (12)	75 (24)
C(17)	-41531 (28)	7549 (58)	-16261 (16)	225 (23)	1178 (83)	61 (8)	23 (38)	21 (11)	4 (23)
C(18)	-48206 (29)	-17955 (55)	-10197 (17)	296 (25)	851 (75)	92 (9)	-137 (37)	35 (12)	-45 (22)
C(19)	75363 (28)	60211 (51)	9752 (17)	241 (24)	544 (67)	93 (9)	10 (34)	30 (11)	16 (21)
O(1)	12938 (19)	-33254 (43)	23308 (12)	284 (18)	1151 (59)	124 (7)	144 (30)	-39 (8)	-32 (18)
O(2)	-49756 (19)	1590 (41)	-22160 (11)	294 (17)	1210 (63)	84 (6)	138 (28)	1 (8)	-11 (16)
S(1)'	51404 (7)	67831 (16)	56471 (4)	174 (5)	1032 (19)	109 (2)	18 (9)	25 (3)	-46 (6)
S(2)'	61167 (7)	45381 (15)	61241 (4)	251 (6)	819 (18)	99 (2)	-86 (9)	48 (3)	-3 (6)
C(1)'	63294 (27)	83974 (55)	57960 (17)	230 (23)	721 (72)	97 (9)	-74 (36)	35 (12)	-13 (22)
C(2)'	65366 (28)	93741 (56)	64709 (18)	253 (24)	858 (81)	116 (9)	-108 (38)	30 (12)	-61 (23)
C(3)'	69481 (29)	81112 (59)	70721 (18)	300 (25)	1175 (88)	95 (9)	-59 (39)	36 (12)	-79 (23)
C(4)'	77717 (28)	66187 (61)	69851 (17)	258 (24)	111 (82)	81 (8)	-51 (41)	-12 (11)	18 (24)
C(5)'	74981 (27)	57605 (54)	62888 (16)	175 (22)	843 (75)	87 (9)	-93 (35)	10 (11)	8 (23)
C(6)'	83727 (27)	42982 (55)	62601 (17)	215 (23)	905 (80)	95 (8)	28 (36)	26 (11)	39 (22)
C(7)'	82181 (27)	34811 (57)	55693 (18)	226 (24)	850 (74)	114 (9)	116 (37)	39 (12)	31 (23)
C(8)'	80941 (26)	49453 (55)	50300 (16)	172 (21)	780 (75)	94 (8)	26 (34)	27 (11)	38 (22)
C(9)'	71378 (27)	63094 (55)	50417 (17)	182 (22)	975 (83)	94 (9)	-7 (36)	26 (11)	13 (22)
C(10)'	73464 (26)	72675 (53)	57379 (16)	158 (22)	740 (75)	97 (8)	-38 (33)	30 (11)	42 (21)
C(11)'	68820 (30)	76870 (63)	44577 (18)	399 (27)	1091 (83)	102 (9)	284 (43)	74 (12)	98 (25)
C(12)'	66516 (29)	67150 (66)	37812 (17)	325 (26)	1486 (90)	85 (9)	112 (45)	42 (12)	135 (26)
C(13)'	76151 (27)	54083 (57)	37652 (17)	215 (24)	1092 (81)	93 (9)	43 (36)	52 (12)	52 (23)
C(14)'	78040 (27)	40396 (56)	43442 (17)	182 (23)	1008 (80)	107 (9)	-85 (34)	33 (11)	-26 (22)
C(15)'	86001 (29)	25810 (62)	41957 (17)	355 (27)	1060 (80)	111 (9)	-37 (43)	71 (13)	34 (26)
C(16)'	82712 (31)	25163 (68)	34244 (18)	382 (28)	1428 (91)	126 (10)	-42 (46)	75 (13)	-109 (29)
C(17)'	73658 (30)	39945 (64)	31923 (18)	301 (25)	1683 (101)	94 (9)	-164 (42)	58 (12)	-11 (25)
C(18)'	86599 (29)	65402 (64)	37688 (18)	313 (26)	1317 (90)	118 (10)	-190 (43)	71 (13)	4 (26)
C(19)'	83855 (29)	85087 (58)	58757 (18)	236 (24)	944 (79)	119 (10)	-115 (38)	30 (12)	27 (24)
O(1)'	60276 (20)	73213 (41)	72745 (12)	396 (19)	1230 (66)	101 (6)	-98 (30)	86 (9)	-77 (18)
O(2)'	73358 (20)	47113 (55)	25514 (11)	369 (18)	2076 (71)	85 (6)	-63 (36)	70 (9)	38 (21)

\* Coordinate fixed to define origin.

proton acceptors [O(2) in (Ia) and O(1) in (Ib)]. In the crystal, the molecules form continuous intermolecular hydrogen-bonded chains. Each chain is arranged in a left-handed helix parallel to the *b* axis containing four molecules [two (Ia) and two (Ib)] in each turn. There are no unusual intermolecular contacts, and the shortest intermolecular S ··· S distance is 4.113 (2) Å.

Torsional angles for (Ia), (Ib) and (II) are compared in Fig. 3. The major difference between (Ia) and (Ib) is

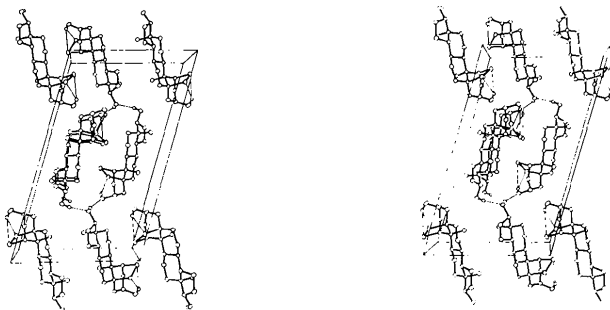


Fig. 1. Unit-cell packing showing hydrogen bonds. View is down *b* with *a* horizontal. Molecules along the lines  $z = 0$  and  $z = 1$  are (Ia), while those at  $z = \frac{1}{2}$  are (Ib). H atoms not involved in hydrogen bonds have been omitted for clarity.

Table 4. Bond distances in the molecules (Å)

	Molecule Ia	Molecule Ib
C(1)–C(2)	1.527 (5)	1.536 (5)
C(1)–C(10)	1.557 (5)	1.542 (5)*
C(1)–S(1)	1.862 (4)	1.842 (4)*
C(2)–C(3)	1.538 (5)	1.522 (5)*
C(3)–C(4)	1.544 (5)	1.534 (6)
C(3)–O(1)	1.441 (4)	1.449 (4)
C(4)–C(5)	1.534 (5)	1.533 (5)
C(5)–C(6)	1.535 (5)	1.531 (5)
C(5)–C(10)	1.553 (5)	1.558 (5)
C(5)–S(2)	1.871 (4)	1.879 (4)
C(6)–C(7)	1.526 (5)	1.525 (5)
C(7)–C(8)	1.523 (5)	1.523 (5)
C(8)–C(9)	1.549 (5)	1.552 (5)
C(8)–C(14)	1.528 (5)	1.527 (5)
C(9)–C(10)	1.557 (5)	1.569 (5)
C(9)–C(11)	1.540 (5)	1.539 (5)
C(10)–C(19)	1.530 (5)	1.534 (5)
C(11)–C(12)	1.533 (5)	1.535 (6)
C(12)–C(13)	1.526 (5)	1.535 (5)
C(13)–C(14)	1.548 (5)	1.530 (5)*
C(13)–C(17)	1.536 (5)	1.539 (6)
C(13)–C(18)	1.531 (5)	1.537 (5)
C(14)–C(15)	1.524 (5)	1.538 (6)
C(15)–C(16)	1.541 (5)	1.553 (5)
C(16)–C(17)	1.547 (5)	1.529 (6)*
C(17)–O(2)	1.432 (4)	1.431 (5)
S(1)–S(2)	2.104 (2)	2.101 (2)

\* Equivalent bond lengths  $d$ , with  $|d_a - d_b| / (d_a^2 + d_b^2)^{1/2} > 2.0$ .

Table 3. Hydrogen fractional coordinates ( $\times 10^4$ ) and thermal parameters ( $\times 10$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub>
H(1B)*	-619 (29)	-4842 (61)	515 (18)	18 (8)	H(1B)'	6130 (26)	9243 (53)	5472 (16)	11 (7)
H(2A)	-627 (31)	-6051 (64)	1514 (18)	26 (9)	H(2A)'	7032 (30)	10364 (62)	6458 (18)	24 (9)
H(2B)	525 (25)	-5963 (53)	1491 (16)	10 (7)	H(2B)'	5864 (27)	9941 (58)	6485 (16)	15 (7)
H(3B)	104 (26)	-4782 (51)	2483 (15)	7 (7)	H(3B)'	7353 (28)	8792 (55)	7431 (17)	14 (7)
H(4B)	-1334 (30)	-2855 (63)	2185 (19)	24 (9)	H(4A)'	7869 (25)	5650 (50)	7316 (15)	4 (6)
H(4A)	-387 (27)	-1420 (54)	2405 (16)	9 (7)	H(4B)'	8487 (28)	7101 (57)	7079 (17)	16 (8)
H(6B)	-2501 (27)	-410 (61)	1624 (17)	15 (7)	H(6B)'	9102 (25)	4896 (54)	6402 (15)	6 (6)
H(6A)	-1564 (30)	1069 (58)	1718 (18)	16 (8)	H(6A)'	8458 (26)	3306 (52)	6600 (16)	7 (7)
H(7B)	-3061 (25)	1892 (52)	787 (15)	3 (6)	H(7A)'	7646 (31)	2893 (67)	5417 (19)	26 (9)
H(7A)	-1953 (28)	1940 (60)	649 (17)	15 (8)	H(7B)'	8896 (27)	2737 (54)	5586 (16)	10 (7)
H(8B)	-3503 (25)	-932 (51)	277 (15)	7 (7)	H(8B)'	8818 (25)	5637 (50)	5125 (15)	4 (6)
H(9A)	-1480 (27)	-1143 (52)	89 (16)	8 (7)	H(9A)'	6478 (29)	5589 (57)	4954 (18)	17 (8)
H(11A)	-1751 (30)	-3710 (61)	-436 (19)	19 (8)	H(11A)'	6243 (31)	8375 (65)	4442 (19)	23 (9)
H(11B)	-2880 (30)	-3929 (60)	-411 (19)	18 (8)	H(11B)'	7488 (34)	8668 (71)	4504 (21)	34 (10)
H(12B)	-3044 (27)	-2794 (55)	-1449 (16)	13 (7)	H(12A)'	6596 (34)	7692 (72)	3427 (20)	31 (10)
H(12A)	-2266 (29)	-1235 (59)	-1194 (17)	16 (8)	H(12B)'	5990 (28)	5950 (57)	3710 (17)	14 (8)
H(14B)	-2632 (28)	1173 (55)	-520 (17)	11 (7)	H(14A)'	7131 (28)	3446 (55)	4297 (16)	11 (7)
H(15B)	-4862 (27)	1662 (57)	-408 (16)	11 (7)	H(15B)'	9402 (26)	2931 (52)	4402 (16)	8 (7)
H(15A)	-3951 (27)	3202 (56)	-317 (16)	12 (7)	H(15A)'	8560 (27)	1384 (54)	4410 (17)	9 (7)
H(16A)	5625 (26)	3590 (52)	8533 (15)	6 (7)	H(16B)'	8912 (29)	2809 (58)	3242 (18)	15 (8)
H(16B)	-5430 (33)	2457 (70)	-1492 (21)	33 (10)	H(16A)'	8049 (30)	1224 (57)	3280 (18)	19 (8)
H(17A)	-3516 (30)	1202 (58)	-1772 (18)	19 (8)	H(17A)'	6665 (25)	3503 (51)	3182 (16)	6 (7)
H(18)1	-5485 (32)	-1129 (66)	-988 (20)	25 (9)	H(18)1'	8565 (30)	7302 (62)	3379 (19)	22 (9)
H(18)2	4913 (30)	7338 (59)	8627 (18)	16 (8)	H(18)2'	8928 (41)	7392 (88)	4126 (25)	49 (13)
H(18)3	-4645 (27)	-2623 (53)	-622 (16)	8 (7)	H(18)3'	9303 (35)	5726 (71)	3765 (22)	32 (10)
H(19)1	-3104 (25)	-3219 (54)	967 (15)	4 (6)	H(19)1'	8323 (27)	9203 (52)	5532 (16)	10 (7)
H(19)2	-2658 (27)	-4899 (58)	644 (17)	13 (8)	H(19)2'	9074 (36)	7840 (72)	5933 (21)	33 (10)
H(19)3	7694 (27)	5347 (53)	1348 (16)	9 (7)	H(19)3'	8508 (42)	9116 (85)	6240 (25)	51 (14)
H(O1)	1396 (34)	-2692 (71)	2031 (21)	37 (10)	H(O1)'	5815 (34)	6392 (75)	7068 (21)	39 (11)
H(O2)	-4913 (38)	-704 (81)	-2342 (22)	48 (12)	H(O2)'	6668 (32)	5002 (71)	2406 (19)	31 (10)

\* Hydrogens are labeled *A* or *B*, corresponding to  $\alpha$ -substituted and  $\beta$ -substituted positions respectively.

found in the conformation of the *D* ring. In (*Ia*) the *D* ring assumes a half-chair conformation with nearly exact  $C_2$  symmetry ( $\varphi_m = 46.9^\circ$ ;  $\Delta = -0.1^\circ$ ) (Altona, Geise & Romers, 1968), while in (*Ib*) a  $\beta$ -envelope is

found ( $\varphi_m = 49.4^\circ$ ;  $\Delta = +29.1^\circ$ ). The conformation of the *D* ring of (*Ia*) extends somewhat the observed range of *D* ring conformation for related 17 $\beta$ -hydroxy androstanes and estranes where the phase angle  $\Delta$  has

Table 5. Bond angles in the molecules ( $^\circ$ )

	Molecule <i>Ia</i>	Molecule <i>Ib</i>		Molecule <i>Ia</i>	Molecule <i>Ib</i>
C(2)–C(1)–C(10)	112.6 (3)	112.8 (3)	C(1)–C(10)–C(9)	112.7 (3)	112.5 (3)
C(2)–C(1)–S(1)	111.2 (2)	111.3 (2)	C(1)–C(10)–C(19)	109.6 (3)	110.3 (3)
C(10)–C(1)–S(1)	107.4 (3)	107.1 (3)	C(5)–C(10)–C(9)	110.6 (3)	109.7 (3)*
C(1)–C(2)–C(3)	115.2 (3)	114.8 (3)	C(5)–C(10)–C(19)	110.6 (3)	110.4 (3)
C(2)–C(3)–C(4)	112.4 (3)	113.7 (3)*	C(9)–C(10)–C(19)	109.5 (3)	109.9 (3)
C(2)–C(3)–O(1)	111.0 (3)	111.6 (3)	C(9)–C(11)–C(12)	113.0 (3)	112.6 (4)
C(4)–C(3)–O(1)	112.2 (3)	111.9 (3)	C(11)–C(12)–C(13)	111.5 (3)	110.9 (3)
C(3)–C(4)–C(5)	116.5 (3)	114.9 (3)*	C(12)–C(13)–C(14)	107.9 (3)	108.9 (3)*
C(4)–C(5)–C(6)	110.6 (3)	110.3 (3)	C(12)–C(13)–C(17)	115.7 (3)	115.9 (3)
C(4)–C(5)–C(10)	111.7 (3)	111.9 (3)	C(12)–C(13)–C(18)	110.3 (3)	110.0 (4)
C(4)–C(5)–S(2)	108.3 (2)	108.0 (2)	C(14)–C(13)–C(17)	99.3 (3)	98.3 (3)*
C(6)–C(5)–C(10)	112.1 (3)	112.9 (3)	C(14)–C(13)–C(18)	113.5 (3)	113.5 (3)
C(6)–C(5)–S(2)	107.6 (3)	107.3 (3)	C(17)–C(13)–C(18)	109.8 (3)	109.8 (3)
C(10)–C(5)–S(2)	106.2 (2)	106.1 (2)	C(8)–C(14)–C(13)	113.7 (3)	114.5 (3)
C(5)–C(6)–C(7)	114.0 (3)	113.8 (3)	C(8)–C(14)–C(15)	119.8 (3)	119.3 (3)
C(6)–C(7)–C(8)	113.3 (3)	113.4 (3)	C(13)–C(14)–C(15)	103.8 (3)	104.1 (3)
C(7)–C(8)–C(9)	110.2 (3)	110.2 (3)	C(14)–C(15)–C(16)	103.3 (3)	103.6 (3)
C(7)–C(8)–C(14)	111.0 (3)	110.5 (3)	C(15)–C(16)–C(17)	106.2 (3)	105.3 (3)*
C(9)–C(8)–C(14)	108.9 (3)	107.9 (3)*	C(13)–C(17)–C(16)	105.5 (3)	104.2 (3)*
C(8)–C(9)–C(10)	111.4 (3)	111.6 (3)	C(13)–C(17)–O(2)	116.2 (3)	116.1 (4)
C(8)–C(9)–C(11)	112.5 (3)	112.6 (3)	C(16)–C(17)–O(2)	108.7 (3)	111.8 (3)*
C(10)–C(9)–C(11)	114.0 (3)	113.5 (3)	C(1)–S(1)–S(2)	93.9 (1)	94.3 (2)
C(1)–C(10)–C(5)	103.7 (3)	103.9 (3)	C(5)–S(2)–S(1)	96.6 (1)	96.0 (1)*

\* See footnote to Table 4.

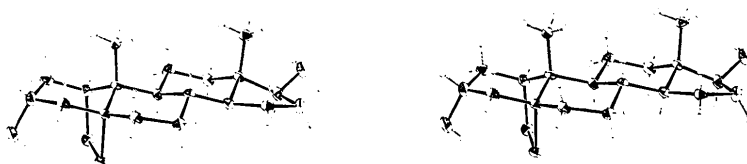


Fig. 2. View of molecule *Ia*. Thermal ellipsoids are drawn at the 50% probability level and H atoms have been assigned an isotropic value of  $1.0 \text{ \AA}^2$  for artistic purposes.

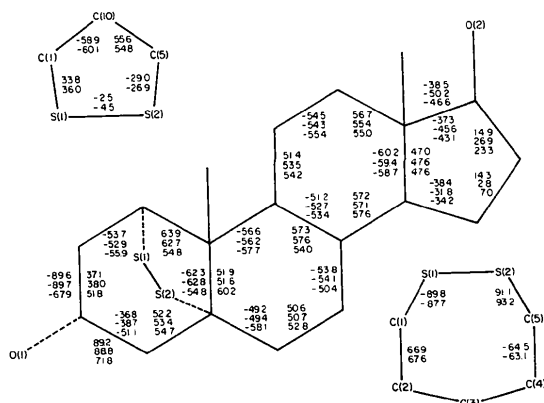


Fig. 3. Torsional angles for (*Ia*) (upper line), (*Ib*) (middle) and (*II*) (lower).

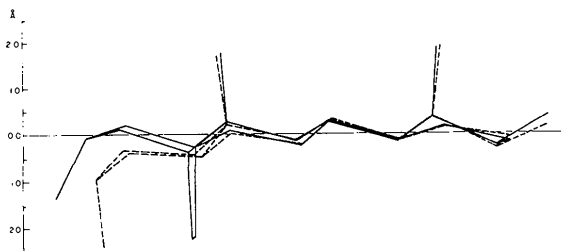


Fig. 4. Skeletal distortions brought about by the addition of the 1,5-diaxial disulfide to 5 $\alpha$ -androsterane-3 $\alpha$ ,17 $\beta$ -diol (*II*). The two molecules [(*Ia*) and (*II*)] have been superimposed by a least-squares fit of the *B*, *C* and *D* rings, omitting C(5), C(6) and C(10). The maximum  $\Delta d$  for the 10 atoms fitted in the least-squares treatment is  $0.067 \text{ \AA}$ , and the  $\Sigma(\Delta d)^2 = 0.012$ . The superimposed molecules are shown fitted to the least-squares plane defined by the androstane skeleton of (*Ia*). Solid lines represent (*Ia*) and dotted lines (*II*).

been limited to the range of values between +9 and +33° (Romers, Altona, Jacobs & de Graaff, 1974; Duax, Weeks & Rohrer, 1976).

In the remainder of the molecule, differences between equivalent torsion angles of (1a) and (1b) are less than 2.3°. Comparing these angles with equivalent angles in (II), however, shows a number of large deviations in the *A* and *B* rings necessary to accommodate the disulfide. These differences in torsion angles indicate a flattening of the *A* ring at the C(2)–C(3)–C(4) region, puckering at C(10), and flattening of the *B* ring at C(5). The opening of valence angles C(1)C(2)C(3), C(3)C(4)C(5), C(5)C(6)C(7), and C(5)C(10)C(9) by 2.5 to 3.7°, the closing of angle C(1)C(10)C(5) by 3.5°, and the lengthening of the C(10)–C(1), C(2)–C(3), and C(3)–C(4) bonds by 0.01 to 0.03 Å [compared with standard values for comparable structures

compiled by Romers *et al.* (1974) and Duax *et al.* (1976)] are correlated with these conformational changes of the rings. The overall conformational change accompanying the replacement of the axial H at C(1) and C(5) in (II) with the epidisulfide to give (I) is shown in the superposition diagram (Fig. 4).

One of the more interesting features of this structure is the close contact or intramolecular hydrogen bond(s) between the S atoms and the 3 $\alpha$ -hydroxyl H(O1) (Table 6). In (1a), where there are no intermolecular hydrogen bonds directed towards O(1), both O(1) and H(O1) lie in the plane of local symmetry and both are an equal distance from S(1) and S(2), with O...S distances equal to the van der Waals contact distance of 3.25 Å [1.85 for S and 1.40 Å for O (Pauling, 1960)] and H...S distances of 2.64 Å. In (1b), H(O1) no longer lies in the plane of local symmetry.

Table 6. *Hydrogen bonds*

<i>D</i> –H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H	H... <i>A</i>	$\angle$ <i>D</i> –H... <i>A</i>
O(1)–H(O1)...S(1)	3.297 (4) Å	0.82 (4) Å	2.65 (4) Å	138 (4)°
O(1)–H(O1)...S(2)	3.246 (4)	0.82 (4)	2.64 (3)	132 (4)
O(1')–H(O1')...S(1')	3.300 (4)	0.80 (4)	2.88 (4)	116 (3)
O(1')–H(O1')...S(2')	3.165 (4)	0.80 (4)	2.50 (5)	141 (4)
O(2)–H(O2)...O(1')	2.766 (4)	0.69 (4)	2.14 (4)	151 (4)
O(2')–H(O2')...O(2)	2.846 (4)	0.83 (4)	2.04 (4)	164 (5)

Table 7. *Bond lengths (Å), bond angles (°) and torsion angles (°) in various disulfides*

	C–S	R* S–S	C–S–S	C–S–S–C	
Gerrardine (ring <i>A</i> )	1.82	2 2.08	96	1†	Gafner & Admiraal (1971)
	1.84	3			
Molecule I	1.852	3 2.103	95.2	–2.5	This work
	1.875	4		–4.5	
Gliotoxin (molecule <i>A</i> )	1.88	4 2.08	98.0	–8.8	Fridrichsons & Mathieson (1967)
Sporidesmin	1.90	4 2.08	98.0	–9.5	Fridrichsons & Mathieson (1965)
Chaetocin	1.88	4 2.077	98.0	+11	Weber (1972)
A26771A	1.90	4 2.068	98.2	11.8	Michel, Chaney, Jones, Hoehn & Nagarajan (1974)
Gliotoxin (molecule <i>B</i> )	1.90	4 2.08	97.7	–15.8	Fridrichsons & Mathieson (1967)
Acetylaranotin (LL-S88 $\alpha$ )	1.882	4 2.082	97	–15.2	Cosulich, Nelson & van den Hende (1968)
				–18.2	
Gerrardine (ring <i>B</i> )	1.82	2 2.06	95	23†	Gafner & Admiraal (1971)
	1.85	3			
1,2-Dithiolane-4-carboxylic acid	1.806	2 2.096	94	27.5	Foss, Hordvik & Sletten (1966)
D,L-6-Thioctic acid	1.79	2 2.053	94	35.0	Stroud & Carlisle (1972)
	1.83	3			
<i>cis</i> -1,2-Dithiane-4,5-diol	1.826	2 2.062	99.1	55.8†	Debaerdemaeker (1975)
				58.1†	
1,2-Dithiane-3,6-dicarboxylic acid	1.85	3 2.07	99	60	Foss, Johnsen & Reistad (1964)
Tetragonal L-cystine	1.814	2 2.043	104.9	+69.3	Chaney & Steinrauf (1974)
L-Cystine. 2HBr. 2H <sub>2</sub> O	1.81	2 2.044	101.2	–80	Rosenfield & Parthasarathy (1975 <i>b</i> )
L-Cystine. 2HCl (neutron)	1.816	2 2.038	103.7	–81.7	Jones, Bernal, Frey & Koetzle (1974)
L-Cystine dimethyl ester. 2HCl. H <sub>2</sub> O	1.807	2 2.045	101.6	–84.4	Vijayalakshmi & Srinivasan (1975)
Dimethyl disulfide (microwave)	1.811	1 2.039	102.7	84.6	Kuhler, Charpentier, Sutter & Dreizler (1974)
Cyclo-L-cystine-acetic acid	1.81	2 2.00	105	–91	Mez (1974)
D-Penicillamine disulfide	1.865	4 2.049	105.5	115	Rosenfield & Parthasarathy (1975 <i>a</i> )

\* *R* is the number of non-hydrogen substituents on the C atom of the S–C bond.

† Calculated from atomic coordinates.

The short S(2)···H(O1) distance in (*Ib*) of 2.50 is considerably shorter than the contact distances of 2.85 obtained when the radius of the polar H is taken as 1.0 Å (Baur, 1972), but compares well with the unusually short S···H(N) distance of 2.43 (13) Å found in penicillamine disulfide (Rosenfield & Parthasarathy, 1975*a*). H(O1) in both (*Ia*) and (*Ib*) is 2.40 Å from the disulfide least-squares plane C(1)S(1)S(2)C(5) and 0.23 Å above the plane normal to the disulfide and intersecting S(1) and S(2). The change in hydrogen bonding from (*Ia*) to (*Ib*) is accompanied by an increase in the torsional angle about the S—S bond from  $-2.5$  to  $-4.5^\circ$ .

On the opposite side of the disulfide plane, the axial H atoms on C(7) and C(9) [H(7A) and H(9A) respectively] make van der Waals contact with S(1) or S(2). H(9A) is slightly closer to S(1) than S(2) with mean distances of 2.68 and 2.73 Å respectively. The mean distance from H(7A) to S(2) is 2.97 Å. Both H(7A) and H(9A) are between 2.30 and 2.40 Å from the least-squares plane defined by the disulfide C(1)S(1)S(2)C(5), and both lie between 1.0 and 1.1 Å above the plane which intersects S(1) and S(2) and is normal to the disulfide plane.

A comparison of the C—S—S—C torsion angles ( $\varphi$ ), S—S and C—S bond lengths, and the C—S—S angles for various disulfides is shown in Table 7. These are mean values for each compound with the following exceptions: (1) the C—S bond lengths are segregated according to the number of non-hydrogen substituents on the C atom; (2) where more than one disulfide is observed, either in crystallographically independent molecules or where two disulfides occur in the same molecule, and these torsion angles are different, both values are given; (3) when the torsion-angle difference is relatively large (gerrardine and gliotoxin) bond lengths and angles for each disulfide are shown. Empirical correlations between  $\varphi$  and the S—S bond length have shown that as  $\varphi$  is closed from about  $90$  to  $0^\circ$ , the S—S bond length increases from about 2.04 to a predicted 2.10 Å (Hordvik, 1970; Jones, Bernal, Frey

& Koetzle, 1974). The S—S bond lengths of 2.104 (2) and 2.101 (2) Å observed for (*Ia*) and (*Ib*) match the prediction exactly. Similar correlations between  $\varphi$  and the C—S bond lengths have been suggested (Jones *et al.*, 1974); however, the data in Table 7 suggest that a more suitable correlation can be made between C—S bond length and the number of non-hydrogen substituents bonded to the C atoms. Thus the mean C—S bond lengths where there are two, three, or four non-hydrogen substituents are 1.812, 1.844 and 1.885 Å respectively. The C—S—S angles are correlated with the size of the smallest ring containing the disulfide. In the 1,2-dithiolanes (five-membered ring), including gerrardine and (*I*), the mean C—S—S angle is  $94.7^\circ$ , while in the 1,2-dithianes and the disulfide-bridged diketopiperazines (six-membered rings) the mean C—S—S angle is  $98.1^\circ$ . For larger rings and acyclic disulfides the mean angle is  $103.5^\circ$ .

Table 8 presents a comparison of the internal torsion angles of the 1,2-dithiolane ring(s) in (*Ia*), (*Ib*), DL-6-thiotoxic acid (*III*) (Stroud & Carlisle, 1972), 1,2-dithiolane-4-carboxylic acid (*IV*) (Foss, Hordvik & Sletten, 1966), and gerrardine [(*Va*) and (*Vb*)] (Gafner & Admiraal, 1971). Three envelope conformations are possible: (1) an  $\alpha$ -envelope where an  $\alpha$ -carbon [either C(1) or C(3) in Table 8] is the out-of-plane atom; (2) a  $\beta$ -envelope where the  $\beta$ -carbon [C(2) in Table 8] is out of the plane; or (3) an *S*-envelope where one of the S atoms is out of the plane. The dithiolane ring in (*III*) is between an *S*-envelope and a half-chair conformation. (*Ia*), (*Ib*) and (*Vb*), with nearly planar disulfides, have the  $\beta$ -envelope conformation of the dithiolane ring, while (*IV*) and (*Va*) adopt an  $\alpha$ -envelope conformation. The mean dithiolane torsion angle for (*I*) of  $36^\circ$ , compared to the mean angle for (*III*), (*IV*) and (*V*) of  $30.7^\circ$ , indicates some distortion in the dithiolane ring of the fused ring system of (*I*).

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Table 8. Torsion angles ( $^\circ$ ) for some 1,2-dithiolanes

	(III)	(IV)	(Va)	(Vb)	(Ia)	(Ib)
C(1)S(1)S(2)C(3)	-34.5	27.5	-23.6	-0.6	-2.5	-4.5
S(1)S(2)C(3)C(2)	20.0	-47.4	44.7	28.5	-29.0	-26.9
S(2)C(3)C(2)C(1)	7.7	53.2	-51.9	-51.4	55.6	54.8
C(3)C(2)C(1)S(1)	-36.3	-29.0	32.1	51.4	-58.9	-60.1
C(2)C(1)S(1)S(2)	43.0	-3.6	-0.3	-27.2	33.8	36.0
Mean	28.3	32.1	30.5	31.5	36.0	36.5

Torsion angles for (*III*), (*IV*) and (*V*) were calculated from the atomic coordinates given in the references listed below. These signs are relative and may not reflect the absolute configuration. (*III*) DL-6-Thiotoxic acid (Stroud & Carlisle, 1972). (*IV*) 1,2-Dithiolane-4-carboxylic acid (Foss, Hordvik & Sletten, 1966). (*Va*), (*Vb*) The two 1,2-dithiolane rings in gerrardine (Gafner & Admiraal, 1971).

## References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.
- BERGSON, G., SJOBERG, B., TWEIT, R. C. & DODSON, R. M. (1960). *Acta Chem. Scand.* **14**, 222–223.
- CHANEY, M. O. & STEINRAUF, L. K. (1974). *Acta Cryst.* **B30**, 711–716.
- COSULICH, D. B., NELSON, N. R. & VAN DEN HENDE, J. H. (1968). *J. Amer. Chem. Soc.* **90**, 6519–6521.
- DEBAERDEMAEKER, T. (1975). *Cryst. Struct. Commun.* **4**, 565–568.
- DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, pp. 271–383. New York: John Wiley.
- FOSS, O., HORDVIK, A. & SLETTEN, J. (1966). *Acta Chem. Scand.* **20**, 1169–1171.
- FOSS, O., JOHNSEN, K. & REISTAD, T. (1964). *Acta Chem. Scand.* **18**, 2345–2354.
- FRIDRICHSONS, J. & MATHIESON, A. McL. (1965). *Acta Cryst.* **18**, 1043–1052.
- FRIDRICHSONS, J. & MATHIESON, A. McL. (1967). *Acta Cryst.* **23**, 439–448.
- GAFNER, G. & ADMIRAAL, L. J. (1971). *Acta Cryst.* **B27**, 565–568.
- GERMAIN, G., MAIN, P. & WOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- HARPP, D. N. & GLEASON, J. G. (1970). *J. Org. Chem.* **35**, 3259–3263.
- HORDVIK, A. (1970). *Quart. Rep. Sulfur Chem.* **5**, 21–43.
- HUFFMAN, J. C. (1974). *A Crystallographic Study of Electron-Deficient Compounds*. Thesis, Indiana Univ., Bloomington, Indiana.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JONES, D. D., BERNAL, I., FREY, M. N. & KOETZLE, T. F. (1974). *Acta Cryst.* **B30**, 1220–1227.
- KUHLER, M., CHARPENTIER, L., SUTTER, D. & DREIZLER, H. (1974). *Z. Naturforsch.* **29a**, 1335–1344.
- MEZ, H.-C. (1974). *Cryst. Struct. Commun.* **3**, 657–660.
- MICHEL, K. H., CHANEY, M. O., JONES, N. D., HOEHN, M. M. & NAGARAJAN, R. (1974). *J. Antibiotics*, **27**, 57–64.
- NEUBERT, L. A. & CARMACK, M. (1974). *J. Amer. Chem. Soc.* **96**, 943–945.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- PRECIGOUX, G., BUSETTA, B., COURSEILLE, C. & HOSPITAL, M. (1972). *Cryst. Struct. Commun.* **1**, 265–268.
- ROMERS, C., ALTONA, C., JACOBS, H. J. C. & DE GRAAFF, R. A. G. (1974). *Terpenoids and Steroids*, Vol. 4, pp. 531–583. London: The Chemical Society.
- ROSENFELD, R. E. JR & PARTHASARATHY, R. (1975a). *Acta Cryst.* **B31**, 462–468.
- ROSENFELD, R. E. JR & PARTHASARATHY, R. (1975b). *Acta Cryst.* **B31**, 816–819.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- STROUD, B. M. & CARLISLE, C. H. (1972). *Acta Cryst.* **B28**, 304–307.
- TWEIT, R. C. & DODSON, R. M. (1959). *J. Amer. Chem. Soc.* **81**, 4409–4412.
- VJAYALAKSHMI, R. K. & SRINIVASAN, R. (1975). *Acta Cryst.* **B31**, 993–998.
- VISSCHER, M. O., HUFFMAN, J. C. & STREIB, W. E. (1974). *Inorg. Chem.* **13**, 792–797.
- WEBER, H. P. (1972). *Acta Cryst.* **B28**, 2945–2951.