The Molecular and Crystal Structures of Two Isomeric Dihydrofukinolidol Sulfites, $C_{15}H_{22}O_5S$

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The molecular and crystal structures of two isomeric dihydrofukinolidol sulfites, $C_{15}H_{22}O_5S$, have been studied by means of an X-ray analysis. The two sulfites, called S-1 and S-2, both crystallize in the orthorhombic space group $P2_12_12_1$, with four molecules in each unit cell. The cell dimensions are $a=12.544$, $b=14.457$, and $c=8.545$ Å for S-1, and $a=12.919$, $b=14.375$, and $c=8.496$ Å for S-2. The reflection intensities were measured visually from equi-inclination integrating Weissenberg photographs taken with Cu$K\alpha$ radiation. The structures were solved by the tangent formula procedure and refined by the block-diagonal-matrix least-squares method, the anisotropic thermal motions being assumed for all the atoms. The final R factor was 10.8% for S-1 and 11.2% for S-2. The absolute configurations of the molecules were determined by using the anomalous dispersion effects of the sulfur atoms for Cu$K\alpha$ radiation. It was found that the six-membered ring containing the sulfite group in S-1 takes the chair conformation, while the same ring in S-2 has the twist boat form. The exocyclic S–O bond in the two sulfites are both axially oriented, and the other corresponding parts of the two isomers are closely similar to each other.

Fukinolidol, $C_{15}H_{22}O_4$, is a hydrolysis product of the sesquiterpenoids, named fukinolide, fukinanolide, and S-fukinolide, which are isolated from the flower stalks of wild butterburs, *Petasites japonicus* Maxim. (Japanese name, "Fuki").[1] The molecular structure of the substance has already been studied by the X-ray method as well as by organic chemical means.[1,2] It has been found that the dihydro derivative of the substance is converted into two isomeric sulfites, $C_{15}H_{22}O_5S$, by the drop-by-drop addition of its pyridine at $-35°$—$-45°C$ over a two-hour period, followed by standing at room temperature for two hours.[3] The isomers, called hereafter S-1 and S-2, are similar in their UV and IR spectra, while they are considerably different in their NMR spectra and solubilities; S-2 is more soluble in polar solvents, such as methanol and chloroform. These facts suggest that the difference in the structure of the two isomers may arise solely from the configuration of the part containing the sulfur atom. Figure 1 shows the structural formula applicable to the two isomers. With respect to the sulfite group, this formula gives four different stereostructures shown in Fig. 2. The purpose of the present work is to determine which of the four structures S-1 and S-2 actually have.

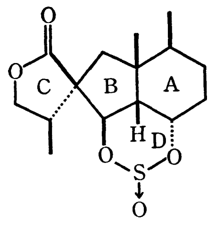

Fig. 1. The molecular structure of dihydrofukinolidol sulfites.

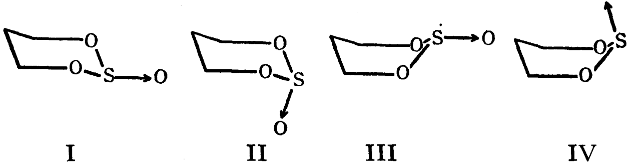

Fig. 2. The four possible stereostructures for the sulfite group.

Experimental

Single crystals of S-1 and S-2 were kindly supplied by Professor Keizo Naya of this university. The crystal data were derived from oscillation and Weissenberg photographs taken with CuK_α radiation; the results are summarized in Table 1. The reflection intensities were measured visually from equi-inclination integrating Weissenberg photographs taken with CuK_α radiation around the a and c axes. For the reflections whose α_1-α_2 doublets were completely split, 1.5 times α_1 spot intensities were used. The Lorentz-polarization and spot-size corrections were made, while the absorption effect was not taken into account, since the crystals used were sufficiently small. These data were then put on an

Table 1. Crystal data

	S-1	S-2
Formula	$C_{15}H_{22}O_5S$	$C_{15}H_{22}O_5S$
MW	314.40	314.40
Mp	190.5—191.5°C (dec.)	187.5—188.5°C (dec.)
Shape	prism	needle
System	orthorhombic	orthorhombic
Cell dimensions		
a	12.544±0.002 Å	12.919±0.002 Å
b	14.457±0.001	14.375±0.002
c	8.545 ±0.002	8.496 ±0.001
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
V	1549.6±0.5 Å^3	1577.8±0.4 Å^3
D_x	1.347 g/cm^3	1.323 g/cm^3

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[1] K. Naya, I. Takagi, M. Hayashi, S. Nakamura, M. Kobayashi, and S. Katsumura, *Chem. Ind.* (London), **1968**, 318.

[2] C. Katayama, A. Furusaki, I. Nitta, M. Hayashi, and K. Naya, This Bulletin, **43**, 1976 (1970).

[3] K. Naya, I. Takagi, and T. Kasai, *ibid.*, **44**, 3204 (1971).

absolute scale by means of Wilson's method: the overall temperature factors obtained were 4.59 Å^2 for S-1 and 4.66 Å^2 for S-2. Thus, the structure factors of 1773 and 1754 independent reflections were derived for S-1 and S-2 respectively.

Structure Determination

The crystal structures of the two sulfites were both elucidated easily by using the tangent formula proce-

TABLE 2. THE WEIGHTING SCHEME FOR S-1 AND THE DISTRIBUTION OF $\langle W\Delta|F_o|^2\rangle$ VALUES

$A = 0.9170\times10^{-3}$ $C = 0.2156$ $E = -0.2750\times10^{2}$
$B = 0.2351\times10^{2}$ $D = -0.4331\times10^{-1}$ $F = 0.6764$

$\lvert F_o\rvert$	sinθ/λ 0.00–0.30	0.30–0.42	0.42–0.49	0.49–0.55	0.55–0.60	0.60–0.64
0.0–5.0	0.380 (4)	0.598 (27)	1.007 (50)	0.882 (138)	0.786 (187)	0.922 (180)
5.0–10.0	0.426 (19)	0.974 (92)	1.282 (108)	1.151 (127)	0.909 (96)	1.119 (61)
10.0–15.0	1.164 (27)	0.840 (101)	1.031 (92)	1.454 (33)	0.023 (6)	
15.0–25.0	0.929 (56)	0.621 (93)	0.562 (47)	0.221 (1)		
25.0–40.0	0.906 (60)	0.499 (30)	0.798 (1)			
40.0–80.0	0.649 (32)	0.409 (1)				

The corresponding numbers of reflections are given in parentheses.

TABLE 3. THE WEIGHTING SCHEME FOR S-2 AND THE DISTRIBUTION OF $\langle W\Delta|F_o|^2\rangle$ VALUES

$A = 0.5503\times10^{-3}$ $C = 0.7144\times10^{-1}$ $E = -0.2420\times10^{2}$
$B = 0.2064\times10^{2}$ $D = 0.5462\times10^{-2}$ $F = 0.6049\times10$

$\lvert F_o\rvert$	sin θ/λ 0.00–0.30	0.30–0.42	0.42–0.49	0.49–0.55	0.55–0.60	0.60–0.64
0.0–5.0	0.350 (7)	0.330 (41)	0.909 (63)	0.830 (155)	1.004 (186)	0.764 (172)
5.0–10.0	0.700 (24)	0.989 (66)	1.045 (112)	1.227 (139)	1.260 (80)	0.985 (54)
10.0–15.0	1.398 (31)	0.981 (104)	1.066 (88)	0.617 (19)	0.952 (8)	
15.0–25.0	0.800 (62)	0.621 (110)	0.668 (45)	3.761 (2)		
25.0–40.0	0.881 (58)	0.668 (22)	0.192 (1)			
40.0–80.0	1.069 (33)					

The corresponding numbers of reflections are given in parentheses.

dure.[4] For the reflections whose E-values were larger than 1.20, the structure factors were calculated with sulfur atom positions obtained from sharpened Patterson functions and with the overall temperature factors previously described. Phase angles with $|F_c|$ values larger than $0.4\times|F_o|$ were selected for the starting set of phases necessary for the tangent formula calculation. This phase calculation was repeated under the condition that the corresponding phases were accepted only when the α-values and the numbers of the correlation terms were larger than 5.0 and 5 respectively. After three cycles of calculation, the accepted phases were increased from 202 to 375 for S-1, and from 204 to 385 for S-2. For both crystals, E-maps calculated with these phases showed clearly the positions of all the atoms except hydrogen. The structures thus obtained were refined by the block-diagonal-matrix least-squares method, first with isotropic temperature factors and then with anisotropic thermal parameters. The following weighting scheme was introduced at this stage:

$$W=\exp(-AX^2-BY^2-CXY-DX-EY-F)$$
$$X=|F_o|,\ Y=\sin\theta/\lambda$$

The intensity data were made into groups with constant intervals along two coordinates, $|F_o|$ and $\sin\theta/\lambda$. The coefficients, A, B, C, D, E, and F, were determined by the least-squares method, so as to give as equal values of $\langle W\Delta|F_o|^2\rangle$ for all the reflection groups as possible. The coefficients thus obtained for S-1 and S-2 and the distributions of $\langle W\Delta|F_o|^2\rangle$ evaluated with these values are, respectively, given

TABLE 4. THE FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS OF S-1

(a) The atomic coordinates

Atom	x/a	σ	y/b	σ	z/c	σ	Atom	x/a	σ	y/b	σ	z/c	σ
S	0.2055	1	0.1190	1	0.7452	1	C(6)	0.0959	4	0.3379	3	0.3380	5
O(1)	0.2336	4	0.0692	2	0.5827	5	C(7)	0.1280	3	0.3456	2	0.5122	4
O(2)	0.2020	3	0.2269	2	0.6920	3	C(8)	0.2381	4	0.3886	3	0.5275	6
O(3)	0.0988	5	0.0950	3	0.7888	5	C(9)	0.1342	3	0.2427	2	0.5561	4
O(4)	0.2416	4	0.4470	4	0.6511	8	C(10)	0.1796	3	0.1951	3	0.4134	5
O(5)	0.3155	3	0.3750	4	0.4503	7	C(11)	0.0593	4	0.4079	2	0.6147	6
C(1)	0.1794	4	0.0914	3	0.4323	6	C(12)	0.1399	6	0.4444	5	0.7335	11
C(2)	0.0720	5	0.0481	3	0.4134	7	C(13)	−0.0331	5	0.3628	4	0.6960	9
C(3)	0.0245	5	0.0795	4	0.2631	7	C(14)	−0.0523	6	0.2137	6	0.1134	7
C(4)	0.0094	4	0.1846	4	0.2570	6	C(15)	0.1840	5	0.2348	5	0.1300	6
C(5)	0.1149	4	0.2367	3	0.2799	4							

(b) The anisotropic temperature factors are in form of $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{23}kl-B_{31}lh)$

Atom	$B_{11}\times10^5$	$B_{22}\times10^5$	$B_{33}\times10^5$	$B_{12}\times10^5$	$B_{23}\times10^5$	$B_{31}\times10^5$
S	1222(10)	401(4)	1485(13)	224(11)	469(14)	−607(22)
O(1)	1128(30)	408(13)	1815(52)	504(34)	38(45)	−333(69)
O(2)	927(22)	321(10)	1167(34)	83(27)	230(32)	−515(51)
O(3)	1526(43)	569(18)	1470(51)	−194(46)	284(49)	669(78)
O(4)	1096(35)	643(22)	3371(113)	−563(47)	−937(87)	−716(107)
O(5)	795(24)	788(25)	2725(84)	−377(42)	1064(80)	21(74)
C(1)	900(32)	352(15)	1560(59)	350(36)	−144(51)	280(75)
C(2)	1091(41)	348(15)	1792(69)	−99(42)	−348(59)	271(92)
C(3)	1005(38)	551(21)	1685(70)	−186(47)	−621(71)	222(97)
C(4)	782(27)	633(22)	1054(44)	102(41)	−388(59)	−108(67)
C(5)	751(26)	483(17)	967(47)	107(36)	148(44)	252(57)
C(6)	977(33)	461(18)	1014(47)	108(41)	387(50)	−181(68)
C(7)	628(21)	290(12)	1188(45)	0(28)	216(42)	−83(54)
C(8)	665(24)	443(17)	1980(72)	−256(37)	458(64)	−235(71)
C(9)	598(20)	282(12)	934(40)	103(26)	116(38)	−46(48)
C(10)	713(25)	352(14)	1034(43)	158(30)	−25(42)	199(57)
C(11)	848(29)	287(14)	1543(58)	83(33)	−233(47)	−354(70)
C(12)	1144(49)	677(30)	2916(140)	−157(65)	−1417(120)	−538(143)
C(13)	933(37)	658(27)	2378(98)	2(53)	−987(89)	788(101)
C(14)	1000(43)	1106(49)	1452(72)	217(78)	−162(99)	−498(98)
C(15)	1040(43)	983(39)	989(53)	18(71)	267(76)	696(82)

The standard deviations are given in parentheses.

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[4] J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).

Table 5. The final atomic parameters and their estimated standard deviations of S-2

(a) The atomic coordinates

Atom	x/a	σ	y/b	σ	z/c	σ	Atom	x/a	σ	y/b	σ	z/c	σ
S	0.2310	1	0.1266	1	0.7429	1	C(6)	0.1115	4	0.3392	3	0.3372	6
O(1)	0.1639	4	0.0650	2	0.6259	5	C(7)	0.1357	3	0.3468	2	0.5173	5
O(2)	0.1765	3	0.2266	2	0.7152	3	C(8)	0.2457	4	0.3795	4	0.5456	8
O(3)	0.3354	4	0.1327	4	0.6799	7	C(9)	0.1269	3	0.2445	2	0.5653	4
O(4)	0.2478	5	0.4363	4	0.6727	9	C(10)	0.1758	3	0.1906	3	0.4317	4
O(5)	0.3213	4	0.3618	4	0.4711	8	C(11)	0.0719	5	0.4157	3	0.6111	7
C(1)	0.1610	4	0.0870	3	0.4532	6	C(12)	0.1465	8	0.4426	5	0.7434	12
C(2)	0.0583	5	0.0499	3	0.3991	8	C(13)	−0.0316	6	0.3829	6	0.6772	9
C(3)	0.0316	5	0.0855	5	0.2339	9	C(14)	−0.0152	7	0.2292	8	0.0771	8
C(4)	0.0260	4	0.1918	4	0.2357	7	C(15)	0.2118	6	0.2337	7	0.1518	7
C(5)	0.1306	4	0.2369	4	0.2820	4							

(b) The anisotropic temperature factors are in form of $\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{23}kl-B_{31}lh)$

Atom	$B_{11}\times 10^5$	$B_{22}\times 10^5$	$B_{33}\times 10^5$	$B_{12}\times 10^5$	$B_{23}\times 10^5$	$B_{31}\times 10^5$
S	1082(9)	489(4)	1326(12)	337(11)	520(14)	−35(22)
O(1)	1284(35)	382(13)	1836(56)	−112(36)	488(46)	−171(84)
O(2)	902(22)	478(13)	933(33)	384(30)	109(36)	−385(50)
O(3)	815(25)	815(25)	2556(80)	435(45)	47(81)	−340(80)
O(4)	1274(45)	672(23)	3957(139)	−613(54)	−577(99)	−1885(139)
O(5)	779(24)	806(25)	3382(112)	−512(44)	1239(98)	−568(93)
C(1)	750(26)	373(15)	1505(58)	141(35)	−387(55)	63(75)
C(2)	843(31)	427(18)	2381(101)	−148(43)	−655(76)	97(105)
C(3)	969(39)	664(28)	2327(105)	197(55)	−1097(104)	−548(126)
C(4)	803(30)	698(26)	1346(62)	31(46)	−685(74)	−269(90)
C(5)	624(21)	643(22)	833(42)	106(38)	67(52)	141(59)
C(6)	738(27)	534(20)	1293(54)	31(40)	559(61)	−400(73)
C(7)	659(22)	309(13)	1376(52)	−114(30)	95(46)	−467(68)
C(8)	775(30)	481(19)	2636(101)	−450(43)	473(80)	−898(102)
C(9)	620(19)	316(13)	958(39)	33(28)	−22(42)	−193(57)
C(10)	585(20)	405(15)	907(40)	57(29)	−100(44)	31(58)
C(11)	1139(42)	343(16)	1778(72)	144(45)	−354(60)	−877(103)
C(12)	1520(70)	612(29)	3063(154)	216(73)	−1363(125)	−1732(204)
C(13)	947(40)	944(42)	2105(98)	722(70)	−1500(116)	−165(111)
C(14)	1125(50)	1407(69)	1407(79)	709(150)	−868(128)	−1027(119)
C(15)	926(40)	1298(57)	1202(61)	290(85)	359(104)	720(91)

The standard deviations are given in parentheses.

in Tables 2 and 3. After several cycles of the refinement using this weighting scheme, the R factor reached a value of 0.108 for S-1 and one of 0.112 for S-2. The final atomic parameters and their standard deviations are given in Tables 4 and 5. The tables of the observed and calculated structure factors are preserved by the Chemical Society of Japan.

The determination of the absolute configurations of the two sulfites was attempted by using the anomalous disperison effect of sulfur atoms for CuK_α radiation ($\Delta f_s''=0.6$). The comparison of the pairs of intensities, hkl and $h\bar{k}l$, was made on the Weissenberg photographs around the a axis already mentioned in the Experimental section. From the data shown in Tables 6 and 7, it can be concluded without any uncertain that the atomic parameters given in Tables 4 and 5, expressed in terms of a right-handed set of axes, correspond to the actual absolute configuration for either of the two sulfites. The absolute configurations of the two isomers thus obtained are both consistent with that of another derivative of fukinolidol.[2)]

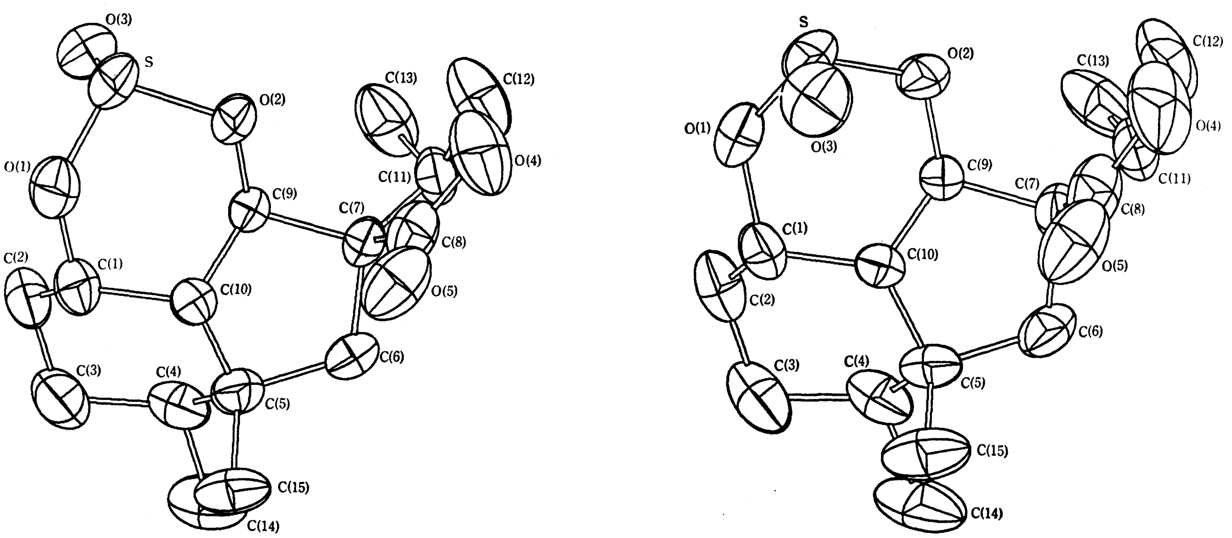
The calculations necessary for the present work were carried out on a FACOM 270—20 computer in this university, using programs written in our laboratory.

Results and Discussion

Molecular Structures. The absolute configurations of the S-1 and S-2 molecules are, respectively, illustrated in Figs. 3(a) and 3(b) where each atom is represented as an ellipsoid, in conformity with the thermal parameters listed in Tables 4 and 5. From these figures, it is found that S-1 and S-2 correspond to II and IV respectively out of the four possible stereostructures given in Fig. 2. The bond distances and

Table 6. Bijvoet inequalities for S-1

h	k	l	$\|F_c(hkl)\|$	$\|F_c(\bar{h}\bar{k}\bar{l})\|$	Observations
1	16	1	2.76	2.46	>
1	16	2	1.07	0.78	>
1	6	6	1.87	1.56	>
1	7	6	5.35	6.43	<
1	8	6	3.05	2.73	>
1	1	7	7.37	5.90	>
1	7	7	7.34	6.56	>
1	9	7	2.43	2.96	<
1	1	8	5.55	4.32	>
1	2	9	3.34	3.70	<
1	4	9	2.09	1.71	>
1	1	10	2.08	2.44	<
1	3	10	2.60	2.32	>
1	6	10	3.11	2.71	>
2	13	1	4.76	3.81	>
2	14	1	6.44	5.77	>
2	16	1	5.27	4.67	>
2	14	2	5.17	4.54	>
2	16	2	4.97	4.40	>
2	17	3	3.78	4.43	<
2	5	4	7.21	6.16	>
2	11	4	3.02	3.94	<
2	16	4	3.48	4.15	<
2	6	5	9.67	11.56	<
2	9	6	5.16	5.83	<
2	7	8	2.63	3.08	<
3	5	1	10.93	9.43	>
3	7	1	17.33	15.39	>
3	8	1	4.65	6.50	<
3	11	1	4.53	3.27	>
3	1	2	7.41	9.35	<
3	2	2	6.98	9.84	<
3	8	3	17.09	19.04	<
3	12	3	10.80	11.96	<
3	15	3	3.20	2.64	>
3	16	3	5.26	5.97	<
3	12	4	6.49	7.21	<
3	5	5	3.05	4.01	<
3	1	7	5.83	4.91	>
3	5	7	3.74	4.50	<
3	1	9	2.19	2.75	<
4	6	1	3.86	2.42	<
4	7	1	8.12	9.25	<
4	13	1	7.93	6.64	>
4	12	2	6.86	7.81	<
4	5	3	5.26	7.61	<
4	1	4	9.74	7.96	>
4	5	5	3.68	1.82	>
4	8	6	3.12	2.45	>
4	9	6	2.29	3.06	<
4	2	9	2.48	2.02	>
5	13	1	2.95	3.26	<
5	14	1	3.41	2.75	>
5	2	2	27.29	30.25	<
5	12	2	5.39	6.06	<
5	4	3	5.48	2.69	>
6	3	2	13.11	11.00	>
6	11	2	10.63	11.99	<
6	15	2	5.90	5.22	>
6	12	3	1.82	2.14	<
6	3	5	10.38	9.11	>
6	1	10	3.31	2.95	>
7	12	1	7.00	6.24	>
7	14	2	4.71	4.21	>
7	13	4	1.53	1.89	<
7	14	4	2.49	1.70	>
7	12	5	5.60	6.30	<



(a) S—1 (b) S—2

Fig. 3. The molecular frameworks.
The thermal ellipsoids enclose 50% probability.

TABLE 7. BIJVOET INEQUALITIES FOR S-2

h	k	l	$\lvert F_c(hkl)\rvert$	$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$	Observations	h	k	l	$\lvert F_c(hkl)\rvert$	$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$	Observations
1	5	1	2.28	4.74	<	4	5	4	2.12	1.13	>
1	11	1	4.77	5.91	<	4	11	4	5.12	4.42	>
1	13	2	4.21	3.45	>	4	15	4	1.74	2.20	<
1	7	3	12.58	10.70	>	4	1	5	3.50	4.35	<
1	8	3	2.18	1.67	>	4	5	5	6.01	6.85	<
1	9	3	10.96	12.21	<	4	9	6	4.01	3.41	>
1	15	3	2.12	2.63	<	4	13	6	2.92	2.45	>
1	17	3	3.96	3.44	>	4	7	7	3.45	2.77	>
1	1	4	13.65	11.19	>	5	9	1	10.92	12.22	<
1	5	4	8.43	7.61	>	5	13	1	2.61	3.80	<
1	13	4	3.60	4.16	<	5	15	1	2.94	3.40	<
1	15	4	1.85	0.92	>	5	16	1	2.55	3.00	<
1	16	4	2.29	2.03	>	5	2	2	3.00	1.85	>
1	17	4	2.27	1.81	>	5	14	2	1.88	2.39	<
1	3	5	7.22	5.91	>	5	3	3	8.72	7.11	>
1	5	6	4.90	6.15	<	5	5	3	4.25	6.13	<
1	9	6	8.36	9.41	<	5	11	3	5.12	4.55	>
1	10	6	2.95	2.47	>	5	11	4	4.24	5.15	<
1	5	7	6.59	7.36	<	5	13	4	4.95	4.45	>
1	6	7	3.17	3.75	<	5	3	6	1.21	2.46	<
1	9	7	4.36	3.93	>	5	6	6	6.83	7.74	<
1	11	7	1.67	2.21	<	6	10	1	10.65	9.36	>
1	12	7	2.17	2.62	<	6	8	2	9.14	7.91	>
1	13	7	4.88	5.43	<	6	15	2	3.47	4.07	<
2	17	2	1.91	2.16	<	6	10	3	6.19	7.28	<
2	16	4	4.31	5.06	<	6	13	3	4.44	4.93	<
2	6	5	7.74	9.38	<	6	15	3	1.95	1.49	>
2	6	7	13.87	12.12	>	6	1	4	4.84	3.93	>
3	14	2	3.69	4.12	<	6	6	5	5.27	3.87	>
3	3	3	10.96	8.65	>	6	7	5	8.29	7.49	>
3	11	3	2.68	1.64	>	6	9	5	6.00	6.81	<
3	13	3	3.72	5.02	<	6	7	6	5.78	6.47	<
3	15	3	2.18	1.54	>	6	1	7	3.27	4.07	<
3	3	4	14.65	16.93	<	6	5	8	3.47	3.96	<
3	6	5	1.23	1.73	<	7	9	1	4.41	5.33	<
3	3	6	8.85	10.35	<	7	1	2	6.33	7.37	<
3	4	8	5.06	5.65	<	7	3	2	5.21	4.69	>
4	12	1	3.30	3.66	<	7	11	2	4.36	3.53	>
4	13	1	6.22	5.56	>	7	9	3	2.95	1.85	>
4	16	1	1.69	1.47	>	8	2	1	4.71	3.90	>
4	3	2	3.96	5.15	<	8	9	1	8.27	7.25	>
4	8	2	14.58	12.65	>	8	2	3	4.17	3.59	>
4	11	2	5.91	6.63	<	8	1	6	4.86	4.36	>
4	12	2	8.77	10.45	<	8	4	6	5.66	4.90	>
4	1	3	8.30	9.49	<						

angles calculated with the final parameters are given in Tables 8 and 9, together with their standard deviations. The correction for the thermal motions of the atoms has been made, on the assumption of the riding motion, by means of the Busing-Levy method.[5] If the standard deviations are taken into consideration, the corresponding values of the bond distances and angles in the S-1 and S-2 molecules are in good agreement with each other, in particular for parts remote from the sulfite group. In both S-1 and S-2 molecules, the D rings containing the sulfite group are *cis*-fused with the A ring and *trans*-fused with the B ring, while the A and B rings are joined to each other in the *cis* configuration. On the other hand, the D ring makes a spiro-union with the B ring, the spiro-atom being C(7).

It has been already reported that the six-membered ring of trimethylene sulfite (TSU), like that of 2,2′-dichlorotrimethylene sulfite (DCT), has the chair conformation with the exocyclic S–O bond pointing

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[5] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

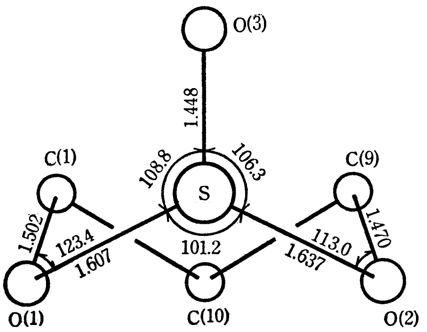
Table 8. The bond distances (Å) in the S-1 and S-2 molecules

	S-1		S-2	
Bond	Distance	e.s.d.	Distance	e.s.d.
S-O(1)	1.603 (1.607)[a]	0.004	1.588 (1.598)	0.005
S-O(2)	1.625 (1.637)	0.003	1.618 (1.626)	0.004
S-O(3)	1.432 (1.448)	0.006	1.455 (1.476)	0.005
O(1)-C(1)	1.489 (1.502)	0.007	1.502 (1.521)	0.006
O(2)-C(9)	1.457 (1.470)	0.005	1.449 (1.464)	0.005
O(4)-C(8)	1.353 (1.394)	0.008	1.354 (1.393)	0.010
O(4)-C(12)	1.457 (1.459)	0.010	1.443 (1.450)	0.012
O(5)-C(8)	1.190 (1.215)	0.007	1.192 (1.215)	0.008
C(1)-C(2)	1.495 (1.504)	0.008	1.502 (1.517)	0.008
C(1)-C(10)	1.508 (1.519)	0.005	1.514 (1.525)	0.005
C(2)-C(3)	1.487 (1.490)	0.008	1.533 (1.544)	0.010
C(3)-C(4)	1.533 (1.545)	0.007	1.530 (1.546)	0.009
C(4)-C(5)	1.535 (1.542)	0.007	1.549 (1.562)	0.007
C(4)-C(14)	1.510 (1.536)	0.008	1.545 (1.579)	0.010
C(5)-C(6)	1.563 (1.567)	0.006	1.562 (1.566)	0.007
C(5)-C(10)	1.524 (1.528)	0.006	1.550 (1.558)	0.006
C(5)-C(15)	1.547 (1.573)	0.007	1.526 (1.560)	0.008
C(6)-C(7)	1.546 (1.560)	0.006	1.566 (1.574)	0.006
C(7)-C(8)	1.521 (1.538)	0.006	1.516 (1.540)	0.007
C(7)-C(9)	1.536 (1.540)	0.005	1.530 (1.537)	0.005
C(7)-C(11)	1.524 (1.533)	0.006	1.515 (1.532)	0.007
C(9)-C(10)	1.512 (1.520)	0.005	1.512 (1.515)	0.005
C(11)-C(12)	1.527 (1.561)	0.010	1.531 (1.564)	0.012
C(11)-C(13)	1.500 (1.525)	0.008	1.525 (1.542)	0.010

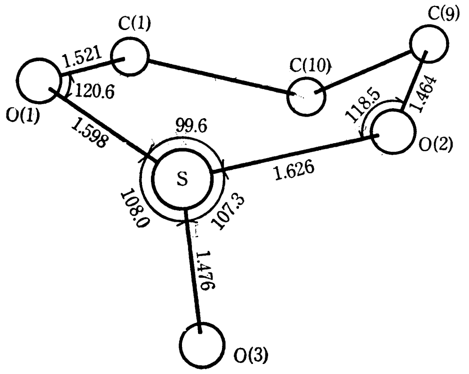
[a] The numerical values in parentheses show the bond lengths corrected for the thermal motion effect.

Table 9. The valency angles (°) in the S-1 and S-2 molecules

	S-1		S-2			S-1		S-2	
	Angle	e.s.d.	Angle	e.s.d.		Angle	e.s.d.	Angle	e.s.d.
O(1)-S-O(2)	101.2	0.2	99.6	0.2	C(5)-C(6)-C(7)	109.5	0.3	109.1	0.4
O(1)-S-O(3)	108.8	0.3	108.0	0.3	C(6)-C(7)-C(8)	110.5	0.3	111.4	0.4
O(2)-S-O(3)	106.3	0.3	107.3	0.2	C(6)-C(7)-C(9)	100.3	0.3	100.3	0.3
S-O(1)-C(1)	123.4	0.3	120.6	0.3	C(6)-C(7)-C(11)	116.7	0.3	116.8	0.4
S-O(2)-C(9)	113.0	0.2	118.5	0.3	C(8)-C(7)-C(9)	109.2	0.3	109.0	0.3
C(8)-O(4)-C(12)	109.5	0.5	110.6	0.6	C(8)-C(7)-C(11)	102.8	0.3	102.9	0.4
O(1)-C(1)-C(2)	114.5	0.4	104.3	0.4	C(9)-C(7)-C(11)	117.4	0.3	116.6	0.4
O(1)-C(1)-C(10)	107.8	0.4	108.7	0.4	O(4)-C(8)-O(5)	120.7	0.5	122.4	0.6
C(2)-C(1)-C(10)	114.0	0.4	115.1	0.4	O(4)-C(8)-C(7)	110.6	0.5	109.5	0.6
C(1)-C(2)-C(3)	109.0	0.5	111.1	0.5	O(5)-C(8)-C(7)	128.7	0.4	128.2	0.5
C(2)-C(3)-C(4)	112.5	0.5	109.6	0.6	O(2)-C(9)-C(7)	112.1	0.3	111.8	0.3
C(3)-C(4)-C(5)	112.0	0.4	112.3	0.5	O(2)-C(9)-C(10)	110.5	0.3	112.6	0.3
C(3)-C(4)-C(14)	111.6	0.5	110.8	0.5	C(7)-C(9)-C(10)	105.2	0.3	105.1	0.3
C(5)-C(4)-C(14)	114.1	0.4	112.1	0.5	C(1)-C(10)-C(5)	118.1	0.3	118.3	0.3
C(4)-C(5)-C(6)	111.6	0.3	109.4	0.4	C(1)-C(10)-C(9)	111.4	0.3	111.1	0.3
C(4)-C(5)-C(10)	111.2	0·4	111.0	0.4	C(5)-C(10)-C(9)	102.9	0.3	103.8	0.3
C(4)-C(5)-C(15)	111.6	0.4	113.8	0.4	C(7)-C(11)-C(12)	102.3	0.4	102.1	0.5
C(6)-C(5)-C(10)	102.3	0.3	102.6	0.3	C(7)-C(11)-C(13)	116.5	0.4	118.0	0.5
C(6)-C(5)-C(15)	111.4	0.4	110.8	0.4	C(12)-C(11)-C(13)	110.7	0.5	111.1	0.6
C(10)-C(5)-C(15)	108.3	0.4	108.8	0.4	O(4)-C(12)-C(11)	105.5	0.6	104.5	0.7



(a) S-1



(b) S-2

Fig. 4. The geometry of the sulfite group.

in the axial direction.[6,7] It is interesting to see that S-1 closely resembles the two simple sulfites mentioned above with respect to both the ring conformation and the S–O orientation. On the other hand, the D ring in S-2 has the twist boat form, although the exocyclic S–O bond is also axial. The geometries of the sulfite group in S-1 and S-2 are shown in Figs. 4(a) and 4(b) respectively. These bond distances and angles are nearly the same as those in TSU and DCT; the four sulfites are compared in Table 10. In this table, it may be seen that the average C–O distances in S-1 and S-2, 1.486 and 1.493 Å, are somewhat longer than those in TSU and DCT, 1.46 and 1.462 Å, and that the S–O(3) bond in S-2 is slightly lengthened as compared with those in other, similar compounds.

It is noteworthy that, in both S-1 and S-2, the C(1)-O(1) and C(9)-O(2) distances, especially the former (1.502 Å in S-1 and 1.521 Å in S-2) are significantly longer than the accepted values for C–O bonds in ethers and alcohols, 1.43—1.44 Å. An elongation of the C–O bond has already been found in TSU (1.49 and 1.42 Å) and DCT (1.471 and 1.453 Å), but the deviation from the normal value was taken as hardly significant.[7] The large deviation for the C(1)-O(1) bonds found in the two isomeric sulfites can, though, be taken as significant and can be explained as follows. We may suppose that the lone-pair electrons on the sulfur atom are delocalized. It follows that a portion of the electrons on the sulfur atom, distributed over the tetrahedral directions, will be displaced towards the anti-bonding σ-orbital of the C–O grouping. This picture will explain not only the elongation of the C–O bond, but also the fact that the endocyclic S–O bonds are somewhat shortened in comparison with the S–O single bond distance calculated by using Schomaker-Stevenson's method, 1.69 Å. If this view is accepted, and if we compare the lengths of the S–O and C–O bonds for the sulfite groups, it can be concluded that the outflow of the lone-pair electrons on the sulfur atom will be somewhat more in S-2 than in S-1. Consequently, the sulfur atom in S-2 will become more electronegative and will form a weaker dative bond, S→O(3).

It is of great interest to examine why the two dative bonds, S→O(3), in S-1 and S-2 are formed not in the equatorial orientation, but in the axial orientation. There are several conceivable reasons for this. First, the equatorial orientation of the lone-pair orbital on

Table 10. The comparison of the trimethylene sulfite rings in the S-1, S-2, TSU, and DCT molecules

Bond, Angle	S-1	σ	S-2	σ	DCT	σ	TSU
S-O(1)	1.607	0.004	1.598	0.005	1.615	0.006	1.59
S-O(2)	1.637	0.003	1.626	0.004	1.631	0.006	1.60
S-O(3)	1.448	0.006	1.476	0.005	1.442	0.006	1.45
C(1)-O(1)	1.502	0.007	1.521	0.006	1.453	0.010	1.49
C(9)-O(2)	1.470	0.005	1.464	0.005	1.471	0.010	1.42
C(1)-C(10)	1.519	0.005	1.525	0.005	1.523	0.012	1.51
C(9)-C(10)	1.520	0.005	1.515	0.005	1.522	0.011	1.52
O(1)-S-O(2)	101.2	0.2	99.6	0.2	97.8	0.3	100
O(1)-S-O(3)	108.8	0.3	108.0	0.3	107.8	0.3	—
O(2)-S-O(3)	106.3	0.3	107.3	0.2	107.4	0.3	—
S-O(1)-C(1)	123.4	0.3	120.6	0.3	115.8	0.5	116
S-O(2)-C(9)	113.0	0.2	118.5	0.3	116.6	0.5	116
O(1)-C(1)-C(10)	107.8	0.4	108.7	0.4	109.0	0.6	106
O(2)-C(9)-C(10)	110.5	0.3	112.6	0.3	108.5	0.6	111
C(1)-C(10)-C(9)	111.4	0.3	111.1	0.3	110.6	0.6	110

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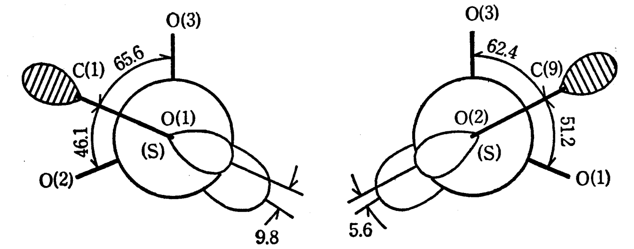
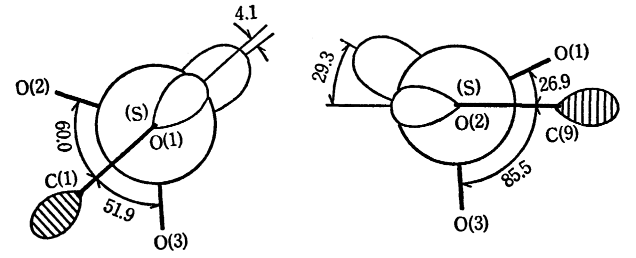
[6] C. Altona, H. J. Geise, and C. Romers, *Rec. Trav. Chim. Pays-Bas*, **85**, 1197 (1966).

[7] J. W. L. van Oyen, R. C. D. E. Hasekamp, G. C. Verschoor, and C. Romers, *Acta Crystallogr.*, **B24**, 1471 (1968).

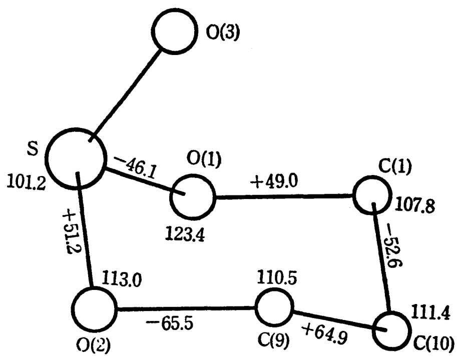


(a) S-1

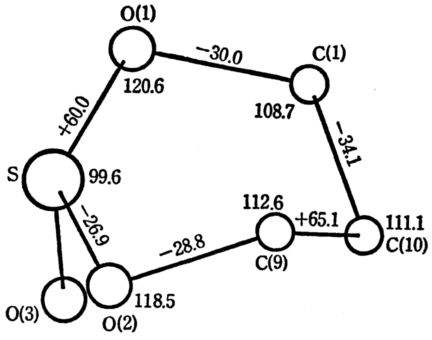


(b) S-2

Fig. 5. The overlapping of the lone-pair orbital on S and the C-O anti-bonding orbitals.



(a) S-1



(b) S-2

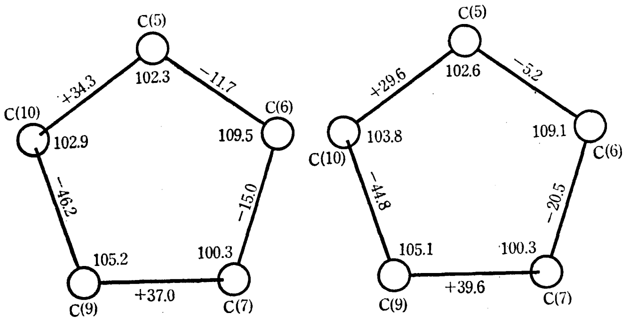
Fig. 6. The valency and torsional angles in D ring.

the sulfur atom is more suitable for the overlapping with the anti-bonding σ-orbital of the C–O groups, as is shown in Fig. 5. Second, if the O(3) atom were equatorially bonded to the sulfur atom, this oxygen atom, carrying a considerable amount of negative charge, would be subjected to a stronger repulsion from the lone-pair electrons on the two oxygen atoms, O(1) and O(2), which, for the major part, would be localized in the sp^3 orbitals and extended axially and equatorially. Third, the attractive interaction between the negatively-charged oxygen atom, O(3), and the more or less positively-charged hydrogen atoms in the neighborhood of the oxygen would make the axial configuration of the S–O(3) bond stable. The distances from the O(3) atom to these hydrogen atoms are: 2.51 Å for H at C(9) and 2.61 Å for H at C(2) in S-1, and 2 54 Å for H at C(10) and 3.12 Å for H at C(1) in S-2 These values are calculated by assuming that the four bonds of the carbon atoms are in the tetrahedral direction and that the C–H distances are 1.08 Å.

It has already been mentioned that the D ring in S-1 takes the chair form. The dihedral angles around the endocyclic bonds in this ring and the internal valency angles are shown in Fig. 6(a). The average dihedral angle, φ, and the average valency angle, θ, are calculated to be 54.9° and 111.2° respectively, while they are 59.2° and 109.8° in TSU and 59.6° and 109.7° in DCT. The values for the latter two substances are in good agreement with the normal values for cyclohexane, 60.0° and 109.5°. On the other hand, both of the φ and θ values for S-1 deviate from the normal values in such a way that the ring becomes less puckered. The two C–O bonds make an angle of about 9° with each other, while the angle formed by the same bonds is found to be about 20° before the formation of the sulfite ring.[2] This shows that the sulfite ring is more or less strained. In fact, the valency angles at the O(1) and O(2) atoms differ from each other by no less than about 10°. Even for such a deformed heterocyclic ring, Altona's relation, $\cos\varphi = -\cos\theta/(1+\cos\theta)$, holds approximately; the calculated value is 55.5°, while the average of the observed dihedral angles is 54.9°.[7]

On the other hand, the twist boat form of the corresponding ring in S-2 is not only the most stable of the flexible forms, but is also suitable for the fusion with the bicyclononane system; the two C–O bond directions make an angle of about 25° with each other differing by only 5° from the angle found before the cyclization. Further, the valency angles at the O(1) and O(2) atoms, 120.6° and 118.5° respectively, are not so different from each other as those in S-1. From the symmetry of the torsional angles shown in Fig. 6(b), it may be seen that the heterocyclic ring in S-2 has roughly a two-fold rotation axis through the O(2) and C(1) atoms, though it is somewhat more flattened than the ideal twist boat form of cyclohexane, where the dihedral angels are 70°39′ or 33°10′.

The conformation of the B ring in S-1 differs from that in S-2; the former takes almost the half-chair form, while the latter has nearly the envelope form. The two ring conformations are illustrated in Fig. 7. In S-1, the C(9) and C(10) atoms deviate above and below from the plane containing the C(5), C(6), and C(7) atoms; the deviations are about 0.39 Å for the C(9) atom lying on the side opposite to the C(15) and about −0.30 Å for the C(10) atom. On the other hand, in S-2, the C(5), C(6), C(7), and C(10) atoms are nearly coplanar, and the C(9) atom deviates by about 0.63 Å toward the same side as the C(4) atom from the mean plane through the first four atoms. Though the five-membered rings in

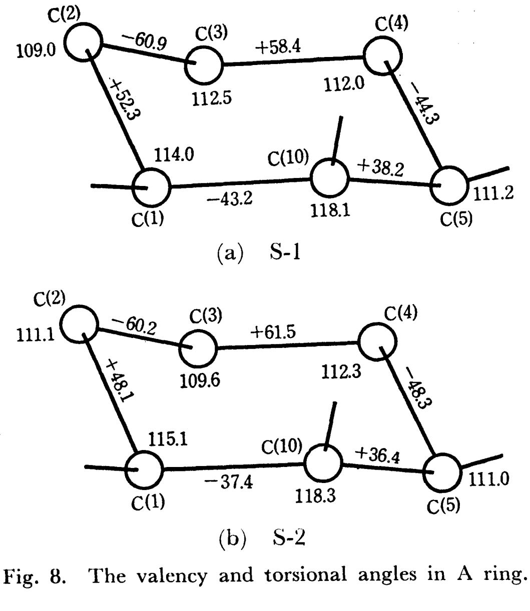


(a) (b)

Fig. 7. The valency and torsional angles in B rings; (a) S-1, (b) S-2.

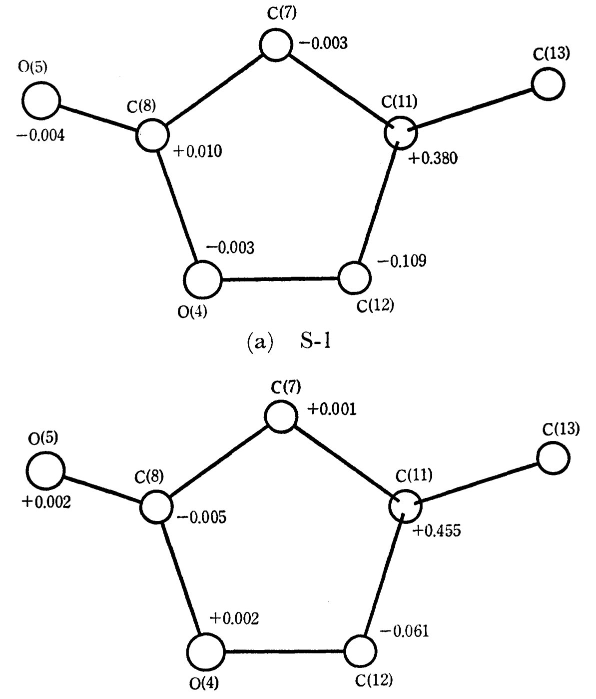
fukinolidol di-bromoacetate as well as in S-2 are found to be approximately of the envelope form, in the former the C(10) atom is considerably displaced from the mean plane through the other four atoms. Thus, the conformation of the five-membered ring varies not only with the fusion of a heterocyclic ring containing the sulfite group, but also with the conformation of the sulfite ring itself.

The conformations of the A rings in S-1 and S-2 are shown in Figs. 8(a) and 8(b) respectively. These two conformations are quite close to each other. This shows that, in the two sulfites, the conformation of the cyclohexane rings is less influenced than that of the cyclopentane rings by the fusion of the sulfite group. The same conclusion can also be drawn from an examination of the conformations around the C(1)-C(10), C(5)-C(10), and C(9)-C(10) bonds. These can be explained by the rigidness of the chair form of the cyclohexane ring. However, a closer examination shows that the A ring is, in fact, affected to some extent by the conformation of the D ring; for example, the difference between the dihedral angles for the C(1)–C(10) bond is found to be about 5.8°. The six-membered rings in the bicyclononane system of S-1 and S-2 are somewaht more flattened than the normal ring of cyclohexane. The averages of the internal valency angles, θ, are 112.8° for S-1 and 112.9° for S-2. The mean values of the dihedral angles, ψ, as calculated by Altona's equation, are 50.8° and 50.4° for S-1 and S-2 respectively, while the observed values are 49.6° and 47.8° respectively.



(b) S-2

Fig. 8. The valency and torsional angles in A ring.



(b) S-2

Fig. 9. The deviations of the atoms from the carbonyl plane.

Out of the four rings present in the S-1 and S-2 molecules, the remaining one is a γ-lactone C ring, which makes a spiro-union with the B ring and takes the envelope form for both of the two isomers. The corresponding bond lengths, valency angles, and torsional angles for the lactone rings of the two molecules are in good agreement with each other within the present limits of experimental error. This may show that the lactone ring is located too far from the sulfite group to be influenced by the conformational

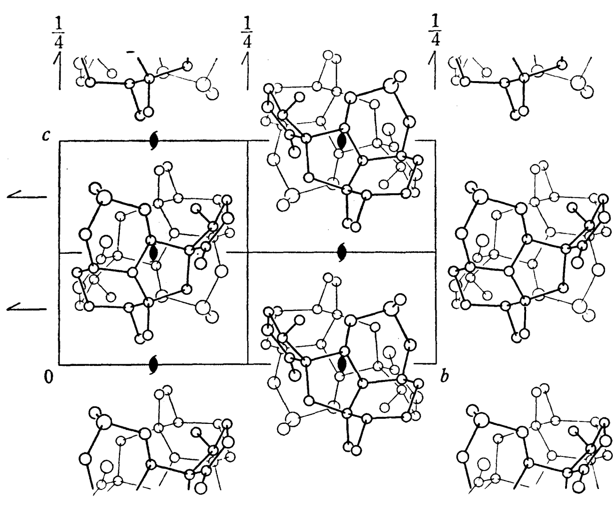


Fig. 10. The crystal structure of S-1 viewed along the a axis.

change of this group. The C(7), C(8), C(12), and O(4) atoms lie nearly on a plane, and the C(11) atom is displaced from the mean plane through the four atoms by about 0.47 Å for S-1 and 0.50 Å for S-2. The deviations of the atoms from the carbonyl plane are illustrated in Fig. 9.

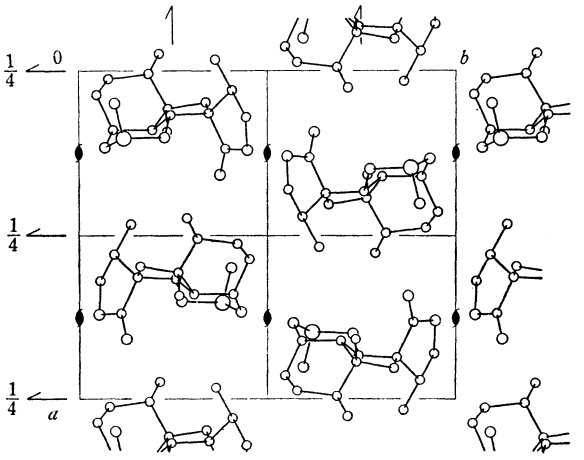


Fig. 11. The crystal structure of S-1 viewed along the *c* axis.

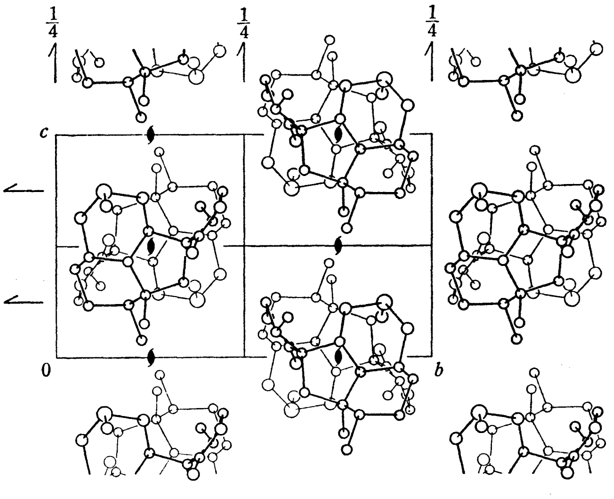


Fig. 12. The crystal structure of S-2 viewed along the *a* axis.

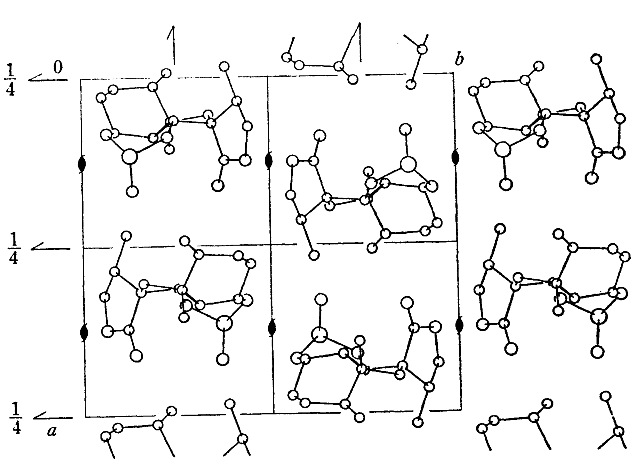


Fig. 13. The crystal structure of S-2 viewed along the *c* axis.

Table 11. The intermolecular contacts in the S-1 crystal

(1)	I···II (III···I)	
	O (5)···C (4)	3.59 Å
	O (5)···C (2)	3.60
	C (10)···C (13)	3.82
	C (1)···C (13)	3.83
	C (8)···C (4)	4.01
	C (8)···C (3)	4.04
	C (15)···C (13)	4.10
(2)	I···IV (V···I)	
	S···C (15)	3.70 Å
	C (13)···C (14)	4.17
(3)	I···VI (VII···I)	
	S···C (1)	3.73 Å
	S···C (2)	3.96
(4)	I···VIII (XII···I)	
	O (3)···C (11)	3.45 Å
	O (3)···C (13)	3.46
	C (2)···C (12)	4.29
(5)	I···IX (XIII···I)	
	C (3)···C (6)	3.90 Å
	C (3)···C (11)	4.21
	C (2)···C (6)	4.28
(6)	I···X (XI···I)	
	C (12)···O (5)	3.25 Å
	C (12)···C (8)	3.81

I: *x*/*a*, *y*/*b*, *z*/*c* (given in Table 4)
II: 1/2+*x*/*a*, 1/2−*y*/*b*, 1−*z*/*c*
III: −1/2+*x*/*a*, 1/2−*y*/*b*, 1−*z*/*c*
IV: *x*/*a*, *y*/*b*, 1+*z*/*c*
V: *x*/*a*, *y*/*b*, −1+*z*/*c*
VI: 1/2−*x*/*a*, −*y*/*b*, 1/2+*z*/*c*
VII: 1/2−*x*/*a*, −*y*/*b*, −1/2+*z*/*c*
VIII: −*x*/*a*, −1/2+*y*/*b*, 3/2−*z*/*c*
IX: −*x*/*a*, −1/2+*y*/*b*, 1/2−*z*/*c*
X: 1/2−*x*/*a*, 1−*y*/*b*, 1/2+*z*/*c*
XI: 1/2−*x*/*a*, 1−*y*/*b*, −1/2+*z*/*c*
XII: −*x*/*a*, 1/2+*y*/*b*, 3/2−*z*/*c*
XIII: −*x*/*a*, 1/2+*y*/*b*, 1/2−*z*/*c*

Table 12. The intermolecular contacts in the S-2 crystal

(1)	I···II (III···I)	
	O (3)···C (14)	3.45 Å
	O (3)···C (13)	3.49
	O (5)···C (2)	3.49
	O (3)···C (6)	3.59
	O (3)···C (4)	3.60
	C (15)···C (13)	3.99
	C (10)···C (13)	4.03
	C (1)···C (13)	4.15
	C (8)···C (3)	4.17
	C (8)···C (2)	4.19
	C (8)···C (4)	4.20
(2)	I···IV (V···I)	
	S···C (15)	3.81 Å
	C (13)···C (14)	4.06
(3)	I···VI (VII···I)	
	O (3)···C(2)	3.50 Å
	S···C (1)	3.82
	S···C (2)	3.95
(4)	I···VIII (XII···I)	
	O (1)···C (13)	3.55 Å
(5)	I···IX (XIII···I)	
	C (3)···C (6)	4.04 Å
	C (3)···C (11)	4.04
	C (2)···C (6)	4.24
(6)	I···X (XI···I)	
	C (12)···O (5)	3.44 Å
	C (12)···C (8)	3.88

I: *x*/*a*, *y*/*b*, *z*/*c* (given in Table 5)
II~XIII: see Table 11.

Crystal Structures. The molecular arrangements viewed along the *a* and *c* axes are, respectively, shown in Figs. 10 and 11 for S-1 and in Figs. 12 and 13 for S-2. As may be seen in these figures, the two crystal structures are so similar to each other that they may be said to be isostructural. It is interesting to see that, notwithstanding the remarkable variation in the structure of the sulfite group, the molecular arrangments do not differ much from each other. The arrangement of the molecular centers is close to a face-centered lattice. The intermolecular contacts of a molecule with its nearest neighbors are listed in

Tables 11 and 12 for S-1 and S-2 respectively. In the S-1 crystal, there are several contacts somewhat closer than the usual van der Waals ones—for example, 3.25 Å for O(5)···C(12′) and 3.73 Å for S···C(1). From the comparison of the intermolecular distances, it may be said that S-1 has a closer molecular packing than S-2, corresponding to the higher density and the higher melting point.

In conclusion, the authors wish to express their thanks to Professor Keizo Naya and Dr. Ichiro Takagi** of this university, for providing them with the samples.

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