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The Crystal and Molecular Structure of 1,2-Benzodithiol-3-one Oxime

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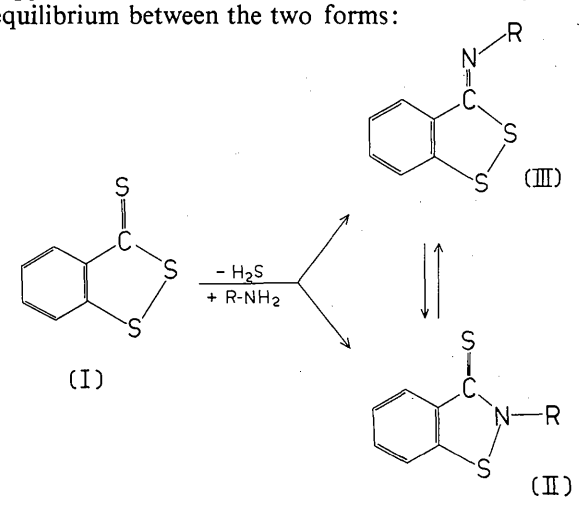
The X-ray analysis of the product obtained by condensing 1,2-benzodithiol-3-thione and hydroxylamine has shown the compound to be 1,2-benzodithiol-3-one oxime, $C_7H_5NOS_2$. The crystal structure has been determined and refined by means of three-dimensional least-squares and Fourier methods (final $R=0{\cdot}094$). Four molecules are contained in the orthorhombic unit cell ($P2_12_12_1$) of dimensions: $a=11{\cdot}979(3)$, $b=15{\cdot}26(2)$, $c=4{\cdot}024(3)$ Å. The two planar benzene and dithiolic rings are nearly coplanar (dihedral angle 177·8°). Bond distances in the dithiolic ring do not indicate any remarkable π delocalization [C–S = 1·74(1), S–S = 2·075(3) Å], nor is conjugation observed for the C=NOH group [C–N = 1·31(1), N–O = 1·42(1) Å] which does not lie exactly in the thiolinone plane (N and O are 0·07 and 0·06 Å out of this plane respectively). The molecules are packed around a 2_1 axis parallel to [001], by a system of O–H···N [2·74(1) Å] strong hydrogen bonds.

Introduction

McClelland & Salkeld (1936) attributed structure (II) to the products obtained by condensing 1,2-benzodithiol-3-thione with primary amines, and correspondingly, structure (III) to the compounds formed with hydrazine, phenylhydrazine and hydroxylamine. They supposed also the existence of an isomeric dynamic equilibrium between the two forms:



This equilibrium is no longer accepted (Schmidt, 1960) and a definite choice between these structures is not easy on the basis of ultraviolet and infrared data (Gialdi & Ponci, 1966).

Therefore X-ray methods have been applied to one of these products, formed by condensation with hydroxylamine, to define the molecular structures of this class of compound which are interesting also for their high antifungal activity (Gialdi & Ponci, 1966). In the present paper are reported the results of this analysis which showed that the molecular structure (III) is present in the crystals.

Experimental

The unit-cell constants measured on single-crystal rotation and Weissenberg photographs are as follows (Cu $K\alpha$, $\lambda=1{\cdot}5418$ Å) (all through the paper the estimated standard deviations are quoted in parentheses and given in units of the last decimal figure):

$C_7H_5NOS_2$ $M=183{\cdot}3$.
$a=11{\cdot}979$ (3), $b=15{\cdot}26$ (2), $c=4{\cdot}024$ (3) Å.
$V=735{\cdot}7$ Å^3, $Z=4$, $d_x=1{\cdot}654$ g.cm^{-3}.
$\mu=57{\cdot}7$ cm^{-1} (Cu $K\alpha$), $F(000)=376$.
Space group: $P2_12_12_1$ (from systematic absences).

Table 1. *Final atomic fractional coordinates* ($\times 10^4$), *thermal parameters* ($\times 10$ Å^2) *with e.s.d.'s and ratios* (*e.s.d.*)/(*coordinate shift*)

	x/a	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}	|r(x)|	|r(y)|	|r(z)|
S(1)	1846 (2)	826 (1)	908 (7)	23 (1)	34 (1)	40 (2)	0 (1)	0 (1)	−2 (2)	∞	2	3
S(2)	647 (2)	−20 (1)	2792 (6)	25 (1)	31 (1)	40 (2)	1 (1)	−2 (1)	0 (2)	9	2	16
O	−1478 (6)	−451 (5)	3853 (22)	27 (3)	34 (2)	48 (6)	1 (4)	6 (6)	0 (5)	15	12	5
N	−1507 (6)	349 (4)	2063 (23)	24 (3)	36 (1)	51 (7)	−1 (4)	1 (6)	−7 (6)	30	20	115
C(1)	891 (9)	1557 (5)	−832 (24)	30 (4)	26 (1)	40 (7)	0 (5)	0 (6)	−3 (6)	4	8	40
C(2)	1256 (10)	2338 (6)	−2343 (27)	34 (4)	33 (2)	38 (7)	−3 (5)	2 (6)	1 (6)	7	6	14
C(3)	461 (12)	2906 (7)	−3612 (31)	40 (5)	40 (2)	46 (9)	−5 (6)	3 (8)	1 (8)	12	∞	22
C(4)	−664 (12)	2705 (7)	−3363 (35)	38 (6)	41 (3)	47 (9)	7 (7)	2 (8)	2 (9)	30	∞	87
C(5)	−1021 (9)	1964 (6)	−1765 (30)	27 (4)	38 (3)	43 (7)	4 (6)	1 (7)	0 (7)	23	4	19
C(6)	−238 (7)	1390 (5)	−431 (24)	25 (3)	29 (2)	39 (6)	−1 (4)	−3 (5)	0 (6)	35	9	7
C(7)	−485 (7)	586 (5)	1340 (26)	24 (3)	30 (2)	39 (6)	−4 (4)	1 (5)	−2 (6)	4	8	8

The e.s.d.'s of cell parameters are derived from a least-squares procedure of refinement applied to powder diffractometer data.

Two series of equi-inclination integrated Weissenberg photographs (filtered Cu radiation, multiple film technique) were taken at room temperature about [100] with levels $h=0,1,\ldots 10$ and about [001] with levels $l=0,1,\ldots 3$. 752 independent reflexions were observed out of a possible 1022. The intensities were measured photometrically and corrected for Lorentz, polarization and spot shape effects. The sample used to take the photographs around [100] was a nearly spherical fragment with a mean radius of 0·015 cm and for this series of data the spherical absorption correction was used. The photographs around [001] were taken using a prism elongated along this axis which was considered to be a cylinder with a mean radius of 0·006 cm in calculating the absorption correction. The two series of data were correlated and put on a common scale using the least-squares procedure of Rollett & Sparks (1960). The absolute scale was determined first by Wilson's (1942) method, then by comparison with the calculated values.

Structure determination and refinement

The coordinates of both sulphur atoms were found first from a three-dimensional Patterson synthesis. The next step was a three-dimensional Fourier synthesis calculated using the phases of the contributions of these atoms to the structure factors ($R=41\%$); this synthesis showed all the non-hydrogen atoms to be well resolved.

The refinement was carried out, first by means of three cycles of least squares using isotropic thermal parameters down to $R=13{\cdot}6\%$, then by six cycles of Booth's differential synthesis with anisotropic thermal parameters. The final residual error indices were (R, for observed reflexions only; R', including $F_o=\frac{1}{2}F_{\min}$ when $F_c\geq F_{\min}$ for unobserved reflexions; multiplicities not considered): $R=9{\cdot}4\%$, $R'=12{\cdot}0\%$, and the ratios between the e.s.d.'s and the shifts of the coordinates were as shown in Table 1 in which the final parameters with their e.s.d.'s (Cruickshank, 1949, 1956) are also quoted. The B_{ij}'s were determined by the method of Nardelli & Fava (1960) using the second derivatives of the electron density from the differential synthesis.

Some attempt was made to locate the hydrogen atoms directly; but while in the final F_o-F_c synthesis the four benzene hydrogen atoms were at the positions expected, assuming a C–H bond length of 1·085 Å, the attempt to locate the oxime hydrogen atom was unsuccessful. In Table 2 the observed fractional coordinates and the electron densities for the benzene hydrogen atoms found in the last differential synthesis are reported. Data for the peaks of the other atoms are given in Table 3. Observed and calculated structure factors (including H atoms – the R value does not change after this inclusion) are compared in Table 4.

Table 2. *Calculated fractional coordinates and electron density values for* H*'s in the benzene group*

	x/a	y/b	z/c	ϱ_0
H(1)	0·2098	0·2454	−0·2647	0·9 e.Å^{-3}
H(2)	0·0706	0·3467	−0·4834	0·8
H(3)	−0·1254	0·3142	−0·4212	1·0
H(4)	−0·1862	0·1846	−0·1495	0·8

The atomic scattering factors used throughout the calculations are those of Dawson (1960) for S, Berghuis,

Table 3. *Atomic peak heights* (e.Å^{-3}), *curvatures* (e.Å^{-5}) *and e.s.d.'s*

		ϱ	$-A_{hk}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
S(1)	obs	32·2	339	301	273	−4	1	6
	calc	32·7	346	312	284	−3	1	6
S(2)	obs	33·6	358	335	293	2	−7	5
	calc	34·2	369	345	303	2	−6	4
O	obs	12·0	113	95	91	−1	6	4
	calc	12·2	116	97	94	−1	5	4
N	obs	10·3	102	91	76	−8	−1	−1
	calc	10·5	105	94	78	−8	−2	0
C(1)	obs	9·0	73	87	74	−6	1	3
	calc	9·1	75	90	77	−6	0	3
C(2)	obs	8·3	65	74	70	−2	1	5
	calc	8·4	68	76	73	−1	1	5
C(3)	obs	7·7	59	71	64	−1	3	−7
	calc	7·9	61	73	66	−1	2	−7
C(4)	obs	7·3	55	60	55	−2	0	4
	calc	7·4	58	61	57	−3	0	4
C(5)	obs	8·5	76	70	65	−2	3	6
	calc	8·6	78	73	67	−1	3	4
C(6)	obs	9·4	90	83	73	−4	−4	7
	calc	9·6	97	86	76	−4	−4	7
C(7)	obs	9·2	95	83	71	−5	2	0
	calc	9·5	98	85	75	−4	1	1
	e.s.d.	0·3	4	3	4	2	2	2

Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for O, N, C and of McWeeny (1951) for H.

All the calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico della Università di Parma using the programs of Nardelli, Musatti, Domiano & Andreetti (1964; 1965) and the least-squares program of Sgarlata (1965).

Discussion

Bond lengths and angles are reported in Table 5 and in Fig. 1. The dithiolic ring is planar, the least-squares plane being:

$$-0{\cdot}0114x+0{\cdot}5159y+0{\cdot}8665z=0{\cdot}9376\ .$$

Table 4. *Observed and calculated structure factors*

A minus sign for F_o means 'less than'.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α°
0	0	2	345	329	180	1	3	2	186	164	207	2	4	1	208	189	307	3	5	1	206	214	25	4	7	1	328	287	196	5	10	2	45-	25	241
0	0	4	90	47	180	1	3	3	205	200	202	2	4	2	261	215	174	3	5	2	227	206	312	4	7	2	55	54	221	5	10	3	76	78	65
0	1	1	461	455	90	1	3	4	45-	35	102	2	4	3	105	75	54	3	5	3	45-	25	282	4	7	3	55-	41	77	5	10	4	28	33	145
0	1	2	29-	4	90	1	3	5	25-	36	216	2	4	4	106	81	275	3	5	4	78	61	71	4	7	4	62-	15	34	5	11	0	75	56	90
0	1	3	34-	0	0	1	4	0	159	152	90	2	4	5	17-	7	321	3	6	0	186	184	270	4	8	0	88	77	0	5	11	1	93	92	347
0	1	4	53-	92	90	1	4	1	275	278	112	2	5	0	127	114	180	3	6	1	225	213	61	4	8	1	164	155	63	5	11	2	133	129	298
0	1	5	29-	20	270	1	4	2	134	124	354	2	5	1	210	255	249	3	6	2	98	80	112	4	8	2	163	157	291	5	11	3	50	48	224
0	2	0	451	568	0	1	4	3	84	91	259	2	5	2	61	66	207	3	6	3	127	126	120	4	8	3	78	71	192	5	11	4	5-	69	62
0	2	1	168	140	180	1	4	4	52	51	253	2	5	3	210	174	0	3	6	4	65	53	222	4	8	4	57-	43	248	5	12	0	47-	19	270
0	2	2	149	142	180	1	4	5	22-	48	50	2	5	4	115	105	85	3	7	0	466	527	90	4	9	0	185	202	180	5	12	1	66	55	166
0	2	3	69	83	180	1	5	0	237	272	270	2	5	5	8-	13	72	3	7	1	158	148	4	4	9	1	240	232	174	5	12	2	105	92	355
0	2	4	53-	23	0	1	5	1	59	72	195	2	6	0	465	520	0	3	7	2	153	142	264	4	9	2	83	80	229	5	12	3	131	124	74
0	2	5	28-	16	0	1	5	2	403	384	202	2	6	1	259	266	240	3	7	3	57	62	84	4	9	3	54-	64	10	5	13	0	47-	3	270
0	3	1	778	837	90	1	5	3	167	159	268	2	6	2	123	106	106	3	7	4	48-	38	186	4	9	4	51-	46	335	5	13	1	72	76	335
0	3	2	213	155	90	1	5	4	55	86	109	2	6	3	151	131	129	3	8	0	250	274	90	4	10	0	50	67	0	5	13	2	98	90	244
0	3	3	144	120	270	1	5	5	37	10	164	2	6	4	41-	18	12	3	8	1	202	205	113	4	10	1	119	114	270	5	13	3	23	24	189
0	3	4	53-	52	90	1	6	0	148	161	270	2	7	0	190	184	0	3	8	2	116	124	56	4	10	2	199	191	265	5	14	0	82	80	90
0	3	5	27-	62	270	1	6	1	270	282	55	2	7	1	177	178	150	3	8	3	46-	15	26	4	10	3	69	76	82	5	14	1	44	48	328
0	4	0	534	676	0	1	6	2	261	254	332	2	7	2	133	119	160	3	8	4	75	95	216	4	10	4	45-	31	249	5	14	2	37-	40	6
0	4	1	382	378	180	1	6	3	237	272	256	2	7	3	209	195	354	3	9	0	313	324	90	4	11	0	111	120	180	5	14	3	46	55	103
0	4	2	617	581	180	1	6	4	47-	59	13	2	7	4	39-	47	53	3	9	1	58	59	151	4	11	1	115	99	186	5	15	0	43-	1	90
0	4	3	127	113	180	1	7	0	48	38	270	2	8	0	306	311	0	3	9	2	215	216	255	4	11	2	62-	31	221	5	15	1	53-	40	26
0	4	4	111	93	0	1	7	1	124	140	156	2	8	1	103	99	290	3	9	3	88	83	269	4	11	3	178	166	9	5	15	2	97	96	227
0	4	5	24-	20	180	1	7	2	129	123	263	2	8	2	245	246	104	3	9	4	81	65	133	4	11	4	34-	36	356	5	16	0	72	81	90
0	5	1	161	144	90	1	7	3	215	199	13	2	8	3	46	56	162	3	10	0	109	100	90	4	12	0	65-	3	0	5	16	1	63	73	306
0	5	2	500	476	270	1	7	4	44-	40	62	2	8	4	37-	53	40	3	10	1	90	73	112	4	12	1	79-	93	298	5	16	2	38	37	37
0	5	3	127	108	270	1	8	0	86	87	90	2	9	0	111	132	0	3	10	2	147	144	100	4	12	2	61-	43	239	5	17	0	77	65	90
0	5	4	50-	38	90	1	8	1	231	245	27	2	9	1	296	308	141	3	10	3	57	58	286	4	12	3	45-	38	118	5	17	1	52	46	151
0	5	5	19-	18	270	1	8	2	165	174	5	2	9	2	125	129	286	3	10	4	53	43	252	4	13	0	66-	23	0	5	17	2	14-	25	225
0	6	0	32-	9	180	1	8	3	170	171	257	2	9	3	40-	17	90	3	11	0	139	126	90	4	13	1	79-	22	319	5	18	0	25-	25	90
0	6	1	111	101	180	1	8	4	43-	8	243	2	9	4	44	51	110	3	11	1	248	242	191	4	13	2	58-	13	279	5	18	1	54	67	304
0	6	2	216	225	180	1	9	0	238	247	90	2	10	0	75	57	0	3	11	2	133	120	236	4	13	3	154	145	355	6	0	0	17-	12	0
0	6	3	54	51	180	1	9	1	213	211	100	2	10	1	120	96	227	3	11	3	76	54	304	4	14	0	90	76	0	6	0	1	100	84	270
0	6	4	134	127	0	1	9	2	124	132	300	2	10	2	209	202	152	3	11	4	30-	44	119	4	14	1	106	101	279	6	0	2	264	239	0
0	7	1	123	108	90	1	9	3	58	74	57	2	10	3	99	104	133	3	12	0	64	70	270	4	14	2	56	62	91	6	0	3	51	42	90
0	7	2	231	222	270	1	9	4	48	69	20	2	10	4	51	44	23	3	12	1	89	68	104	4	14	3	62	54	75	6	0	4	70	69	180
0	7	3	120	103	270	1	10	0	172	159	270	2	11	0	209	196	0	3	12	2	139	147	353	4	15	0	77	79	0	6	1	0	27-	21	0
0	7	4	47-	58	270	1	10	1	216	216	35	2	11	1	388	380	203	3	12	3	93	89	279	4	15	1	129	113	177	6	1	1	436	364	162
0	8	0	30	2	0	1	10	2	66	70	186	2	11	2	102	99	254	3	12	4	31	14	176	4	15	2	40	20	324	6	1	2	202	176	99
0	8	1	167	181	0	1	10	3	70	70	253	2	11	3	37-	11	31	3	13	0	274	256	90	4	15	3	39	43	358	6	1	3	36-	15	216
0	8	2	198	204	180	1	10	4	50	60	112	2	11	4	26-	11	79	3	13	1	122	120	167	4	16	0	57-	34	0	6	1	4	47	43	340
0	8	3	248	238	0	1	11	0	296	299	90	2	12	0	47-	24	160	3	13	2	177	157	286	4	16	1	64-	31	326	6	2	0	224	221	0
0	8	4	144	147	0	1	11	1	87	71	142	2	12	1	145	126	60	3	13	3	36-	25	342	4	16	2	66	71	84	6	2	1	158	135	185
0	9	1	68	52	270	1	11	2	49	16	79	2	12	2	129	138	199	3	14	0	189	199	270	4	17	0	90	89	0	6	2	2	180	160	318
0	9	2	120	123	270	1	11	3	72	64	25	2	12	3	34-	23	182	3	14	1	59	42	128	4	17	1	96	76	155	6	2	3	109	104	139
0	9	3	48	22	90	1	11	4	30-	27	267	2	12	4	29	53	1	3	14	2	54	59	342	4	17	2	29-	20	69	6	2	4	109	107	212
0	9	4	101	97	90	1	12	0	88	89	270	2	13	0	48-	37	180	3	14	3	65	67	285	4	18	0	39-	2	180	6	3	0	80	75	160
0	10	0	101	90	0	1	12	1	172	164	89	2	13	1	162	136	209	3	15	0	53-	6	90	4	18	1	42-	47	90	6	3	1	349	305	132
0	10	1	98	89	0	1	12	2	50	49	211	2	13	2	139	123	254	3	15	1	65-	56	71	4	19	0	20-	1	0	6	3	2	56	45	306
0	10	2	159	160	180	1	12	3	35	41	260	2	13	3	32-	17	253	3	15	2	86	80	310	5	0	1	256	234	90	6	3	3	119	105	352
0	10	3	98	92	0	1	12	4	22-	42	190	2	14	0	173	152	0	3	15	3	61	28	60	5	0	2	379	284	0	6	3	4	35	45	248
0	10	4	37-	43	0	1	13	0	365	364	90	2	14	1	93	72	1	3	16	0	100	92	270	5	0	3	185	174	90	6	4	0	326	311	180
0	11	1	161	164	270	1	13	1	91	82	2	2	14	2	98	97	225	3	16	1	114	95	84	5	0	4	40-	14	180	6	4	1	101	91	229
0	11	2	122	124	90	1	13	2	77	56	297	2	14	3	65	52	26	3	16	2	37-	19	288	5	1	0	341	360	90	6	4	2	187	176	305
0	11	3	41-	8	90	1	13	3	64	57	315	2	15	0	97	69	180	3	17	0	150	139	90	5	1	1	266	243	3	6	4	3	110	83	115
0	11	4	32-	105	90	1	14	0	51-	17	90	2	15	1	227	202	195	3	17	1	50-	45	0	5	1	2	360	340	243	6	4	4	32-	36	208
0	12	0	195	203	0	1	14	1	174	158	148	2	15	2	55	45	211	3	17	2	82	79	283	5	1	3	110	99	105	6	5	0	50	35	0
0	12	1	66-	26	0	1	14	2	49	45	126	2	15	3	54	53	23	3	18	0	36-	19	270	5	1	4	77	84	101	6	5	1	259	243	127
0	12	2	76	50	180	1	14	3	73	69	291	2	16	0	120	115	0	3	18	1	92	78	73	5	2	0	234	212	90	6	5	2	90	93	178
0	12	3	39-	3	180	1	15	0	50-	27	90	2	16	1	112	100	312	3	19	0	61	69	90	5	2	1	292	255	292	6	5	3	160	155	333
0	12	4	55	25	0	1	15	1	62-	30	305	2	16	2	101	95	240	3	19	1	17-	49	26	5	2	2	266	260	26	6	5	4	86	92	268
0	13	1	66-	2	90	1	15	2	44	30	260	2	16	3	4-	45	36	4	0	0	494	560	180	5	2	3	156	148	78	6	6	0	410	407	180
0	13	2	48-	34	90	1	15	3	54	53	306	2	17	0	40	34	0	4	0	1	579	549	270	5	2	4	39-	34	230	6	6	1	169	158	263
0	13	3	36-	13	270	1	16	0	48-	47	90	2	17	1	47-	4	180	4	0	2	190	183	0	5	3	0	549	569	90	6	6	2	51	57	31
0	14	0	265	257	0	1	16	1	152	139	131	2	17	2	74	49	99	4	0	3	137	141	90	5	3	1	274	240	68	6	6	3	55	50	27
0	14	1	65-	27	180	1	16	2	64	62	66	2	18	0	115	111	0	4	0	4	74-	4	180	5	3	2	299	272	231	6	6	4	28-	9	90
0	14	2	46-	34	180	1	16	3	12-	32	308	2	18	1	39-	33	266	4	0	5	27-	15	90	5	3	3	124	120	134	6	7	0	36	31	0
0	14	3	66	68	180	1	17	0	43-	2	90	2	18	2	13-	56	227	4	1	0	324	348	0	5	3	4	92	89	132	6	7	1	120	114	221
0	15	1	94	79	90	1	17	1	60	65	206	2	19	0	25-	28	0	4	1	1	312	296	196	5	4	0	392	439	90	6	7	2	107	106	324
0	15	2	43-	13	270	1	17	2	81	79	277	2	19	1	24-	32	166	4	1	2	78	77	75	5	4	1	174	130	301	6	7	3	88	96	1
0	15	3	41	32	90	1	18	0	37-	7	270	3	0	1	298	281	270	4	1	3	306	312	14	5	4	2	65	64	31	6	7	4	46	61	232
0	16	0	49-	25	0	1	18	1	72	64	95	3	0	2	244	226	0	4	1	4	74-	26	178	5	4	3	49	34	261	6	8	0	257	265	180
0	16	1	59-	33	180	1	18	2	46	64	1	3	0	3	298	285	270	4	1	5	25-	23	185	5	4	4	67	72	226	6	8	1	57	54	271
0	16	2	93	91	180	1	19	0	27-	37	270	3	0	4	57-	35	180	4	2	0	68	76	180	5	5	0	460	474	90	6	8	2	113	97	4
0	16	3	36	47	180	1	19	1	27-	32	130	3	0	5	27-	4	270	4	2	1	368	331	250	5	5	1	256	229	172	6	8	3	77	86	11
0	17	1	53-	34	90	2	0	0	515	659	0	3	1	0	60	42	90	4	2	2	255	223	102	5	5	2	161	148	251	6	8	4	23-	20	126
0	17	2	44	42	270	2	0	1	357	316	90	3	1	1	116	112	144	4	2	3	126	117	98	5	5	3	137	128	82	6	9	0	264	261	0
0	18	0	38-	8	0	2	0	2	234	211	180	3	1	2	266	254	285	4	2	4	73-	75	77	5	5	4	38	40	125	6	9	1	174	161	202
0	18	1	44-	13	0	2	0	3	124	79	90	3	1	3	94	63	40	4	2	5	20-	14	356	5	6	0	90	79	270	6	9	2	72	71	59
0	18	2	59	86	180	2	0	4	62	61	0	3	1	4	151	127	56	4	3	0	433	502	0	5	6	1	292	280	244	6	9	3	77	70	344
0	19	1	30-	54	270	2	0	5	83	87	270	3	1	5	26-	16	76	4	3	1	420	383	183	5	6	2	87	72	166	6	9	4	29	45	241
1	0	1	223	258	90	2	1	0	239	259	180	3	2	0	262	299	270	4	3	2	184	156	2	5	6	3	39-	33	299	6	10	0	147	146	180
1	0	2	267	239	180	2	1	1	162	140	214	3	2	1	286	256	305	4	3	3	139	136	2	5	6	4	76	71	191	6	10	1	119	117	54
1	0	3	122	89	270	2	1	2	260	231	253	3	2	2	180	159	10	4	3	4	72-	88	161	5	7	0	390	390	90	6	10	2	159	144	5
1	0	4	131	111	180	2	1	3	97	83	57	3	2	3	102	89	244	4	4	0	267	310	180	5	7	1	151	142	144	6	10	3	89	98	13
1	0	5	27-	18	90	2	1	4	45-	14	327	3	2	4	93	77	149	4	4	1	168	147	27	5	7	2	178	171	273	6	10	4	11-	53	142
1	1	0	173	221	90	2	1	5	22-	36	159	3	2	5	25-	11	264	4	4	2	197	178	62	5	7	3	42	30	149	6	11	0	57	60	160
1	1	1	363	335	350	2	2	0	170	178	180	3	2	0	266	303	90	4	4	3	90	94	123	5	7	4	33-	29	25	6	11	1	97	82	199
1	1	2	135	126	152	2	2	1	183	162	49	3	2	1	201	175	108	4	4	4	71-	57	131	5	8	0	159	153	270	6	11	2	126	121	74
1	1	3	118	110	291	2	2	2	222	164	167	3	2	2	466	448	328	4	5	0	379	405	0	5	8	1	285	298	233	6	11	3	29-	12	90
1	1	4	50-	18	351	2	2	3	158	121	30	3	2	3	71	56	81	4	5	1	587	561	193	5	8	2	107	95	243	6	12	0	97	89	180
1	1	5	42	50	171	2	2	4	107	90	342	3	3	0	85	97	55	4	5	2	75	62	52	5	8	3	54	56	338	6	12	1	136	117	126
1	2	0	504	631	90	2	2	5	52	68	300	3	3	1	22-	28	212	4	5	3	55-	15	66	5	8	4	70	61	142	6	12	2	116	107	6
1	2	1	1178	1238	101	2	3	0	259	311	180	3	3	2	65	63	270	4	5	4	59-	76	266	5	9	0	127	115	90	6	12	3	25-	24	49
1	2	2	162	153	140	2	3	1	75	70	224	3	4	1	288	267	31	4	6	0	45-	11	0	5	9	1	130	125	233	5	13	0	68	66	180
1	2	3	97	76	250	2	3	2	244	214	151	3	4	2	95	91	292	4	6	1	282	260	128	5	9	2	209	204	324	6	13	1	118	118	177
1	2	4	73	84	190	2	3	3	98	103	319	3	4	3	44-	28	141	4	6	2	55-	29	278	5	9	3	37-	36	265	6	13	2	123	120	111
1	2	5	26-	44	16	2	3	4	116	106	35	3	4	4	107	91	219	4	6	3	74	68	132	5	9	4	56	45	46	6	13	3	21-	15	352
1	3	0	109	98	270	2	3	5	25	46	145	3	4	5	14-	50	137	4	6	4	55-	25	57	5	10	0	95	97	270	6	14	0	65	91	180
1	3	1	525	513	205	2	4	0	307	382	0	3	5	0	375	422	90	4	7	0	142	144	180	5	10	1	78	92	212	6	14	1	44	54	197

Table 4 (*cont.*)

h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°	h	k	l	$\|F_o\|$	$\|F_c\|$	α°
5	14	2	133	124	321	7	12	3	52	49	72	8	12	0	263	261	180	9	14	2	16-	28	283	11	2	3	60	58	64	12	8	2	29	41	106
5	14	3	41	57	161	7	13	0	97	93	90	8	12	1	95	82	179	9	15	0	29-	32	270	11	3	0	50-	33	270	12	9	0	74	78	0
5	15	0	64	69	180	7	13	1	51	49	257	8	12	2	40	38	23	9	15	1	38-	24	73	11	3	1	77-	64	264	12	9	1	126	113	350
5	15	1	54	42	119	7	13	2	30-	5	90	8	12	3	16-	7	23	9	16	0	15-	15	270	11	3	2	136	131	126	12	9	2	74	88	21
5	15	2	27-	23	171	7	13	3	28	35	239	8	13	0	43-	0	0	10	0	0	131	157	180	11	3	3	23-	4	194	12	10	0	34-	16	0
5	16	0	95	99	180	7	14	0	61	48	90	8	13	1	79	84	217	10	0	1	194	185	270	11	4	0	50-	53	90	12	10	1	48-	65	106
5	16	1	75	72	208	7	14	1	161	147	245	8	13	2	45	30	209	10	0	2	160	152	0	11	4	1	90	94	220	12	10	2	7-	56	100
5	16	2	51	62	248	7	14	2	69	67	229	8	14	0	193	196	180	10	0	3	28-	26	270	11	4	2	64	65	112	12	11	0	50	57	0
5	17	0	27-	29	160	7	15	0	33-	40	90	8	14	1	46-	43	305	10	1	0	77	62	0	11	4	3	22-	32	322	12	11	1	76	79	0
5	17	1	22	23	110	7	15	1	72	53	300	8	14	2	83	90	319	10	1	1	253	219	23	11	5	0	167	178	270	12	12	0	44	46	0
6	18	0	98	121	180	7	15	2	45	51	306	8	15	0	33-	22	0	10	1	2	127	120	39	11	5	1	76-	91	167	13	0	1	97	67	90
7	0	1	113	103	270	7	16	0	28-	0	0	8	15	1	83	64	271	10	1	3	28-	31	247	11	5	2	112	103	100	13	0	2	108	109	180
7	0	2	191	163	180	7	16	1	122	125	241	8	15	2	14-	13	352	10	2	0	216	206	180	11	5	3	21-	19	105	13	1	0	45-	7	270
7	0	3	106	112	90	7	17	0	20-	34	270	8	16	0	30	42	180	10	2	1	78-	26	358	11	6	0	49-	19	90	13	1	1	142	123	206
7	0	4	118	119	180	7	17	1	21-	15	357	8	16	1	28-	11	96	10	2	2	156	140	29	11	6	1	161	144	245	13	1	2	93	94	71
7	1	0	139	133	90	8	0	0	468	499	180	9	0	1	396	364	270	10	2	3	51	50	227	11	6	2	38-	25	162	13	2	0	115	114	270
7	1	1	120	106	202	8	0	1	67	62	270	9	0	2	48	29	0	10	3	0	251	252	0	11	6	3	49	55	278	13	2	1	87	71	138
7	1	2	52	49	2	8	0	2	68	73	0	9	0	3	30-	21	90	10	3	1	193	172	358	11	7	0	192	194	270	13	2	2	65	57	212
7	1	3	85	74	242	8	0	3	46	14	270	9	1	0	452	492	270	10	3	2	57	62	61	11	7	1	71-	70	226	13	3	0	42-	44	270
7	1	4	26-	15	230	8	0	4	40	35	0	9	1	1	136	121	115	10	3	3	68	64	112	11	7	2	136	123	28	13	3	1	64-	36	245
7	2	0	93	92	270	8	1	0	33-	22	180	9	1	2	154	154	4	10	4	0	264	279	180	11	7	3	61	43	118	13	3	2	88	88	42
7	2	1	241	209	247	8	1	1	172	148	348	9	1	3	30-	26	188	10	4	1	176	155	127	11	8	0	80	100	270	13	4	0	118	110	270
7	2	2	64	54	250	8	1	2	161	137	295	9	2	0	50	34	270	10	4	2	126	123	55	11	8	1	69-	29	335	13	4	1	165	145	125
7	2	3	81	71	58	8	1	3	64	57	218	9	2	1	380	362	311	10	4	3	78	73	191	11	8	2	34-	32	206	13	4	2	55	48	256
7	2	4	43	54	133	8	1	4	101	102	281	9	2	2	96	66	328	10	5	0	50-	62	180	11	8	3	15	19	305	13	5	0	169	175	270
7	3	0	127	107	90	8	2	0	373	347	180	9	2	3	30-	16	63	10	5	1	116	84	319	11	9	0	159	155	270	13	5	1	59-	68	320
7	3	1	131	111	288	8	2	1	216	188	20	9	3	0	138	121	270	10	5	2	44-	22	323	11	9	1	65-	22	143	13	5	2	64	68	85
7	3	2	54	51	146	8	2	2	155	153	7	9	3	1	78-	20	63	10	5	3	129	134	165	11	9	2	119	113	46	13	6	0	39-	27	270
7	3	3	132	180	241	8	2	3	124	124	8	9	3	2	188	174	59	10	6	0	127	121	180	11	10	0	96	96	270	13	6	1	131	112	104
7	3	4	44	37	32	8	2	4	46	68	225	9	3	3	70	78	121	10	6	1	149	121	53	11	10	1	61-	42	67	13	6	2	32	33	3
7	4	0	150	157	270	8	3	0	87	93	0	9	4	0	243	254	270	10	6	2	79	65	46	11	10	2	36	41	204	13	7	0	148	144	270
7	4	1	199	170	227	8	3	1	311	271	302	9	4	1	264	234	316	10	6	3	51	52	248	11	11	0	100	99	270	13	7	1	77	72	357
7	4	2	156	141	245	8	3	2	44-	41	150	9	4	2	65	59	168	10	7	0	50-	26	180	11	11	1	73	80	238	13	7	2	33	39	158
7	4	3	153	149	115	8	3	3	88	86	59	9	4	3	144	149	119	10	7	1	104	78	299	11	11	2	93	111	71	13	8	0	88	78	90
7	4	4	45	46	54	8	3	4	38	47	274	9	5	0	49-	37	90	10	7	2	57	60	225	11	12	0	33-	17	90	13	8	1	46-	62	68
7	5	0	138	127	270	8	4	0	120	112	180	9	5	1	173	160	52	10	7	3	119	126	169	11	12	1	46-	40	92	13	9	0	122	126	270
7	5	1	41	42	234	8	4	1	88	84	52	9	5	2	173	164	45	10	8	0	87	77	180	11	13	0	85	85	270	13	9	1	38-	31	75
7	5	2	113	105	281	8	4	2	184	167	17	9	5	3	58	70	139	10	8	1	75-	45	65	11	13	1	51	61	350	13	10	0	65	58	90
7	5	3	59	48	180	8	4	3	145	142	10	9	6	0	50-	63	90	10	8	2	115	115	300	12	0	0	49-	29	0	13	10	1	22-	59	10
7	5	4	45	49	94	8	4	4	41	50	167	9	6	1	114	102	261	10	8	3	54	55	299	12	0	1	52	69	90	14	0	0	38-	2	0
7	6	0	37-	27	90	8	5	0	108	117	180	9	6	2	165	154	193	10	9	0	106	106	180	12	0	2	36-	6	0	14	0	1	52-	19	27
7	6	1	168	145	246	8	5	1	128	106	321	9	6	3	108	112	102	10	9	1	156	136	321	12	0	3	45	45	270	14	0	2	91	106	180
7	6	2	165	161	327	8	5	2	247	236	114	9	7	0	50-	4	270	10	9	2	71	64	77	12	1	0	49-	46	180	14	1	0	28-	52	0
7	6	3	116	115	95	8	5	3	26-	21	199	9	7	1	160	150	341	10	9	3	15-	73	144	12	1	1	75-	34	119	14	1	1	106	102	330
7	6	4	33	26	68	8	5	4	25-	14	352	9	7	2	97	85	70	10	10	0	46-	25	0	12	1	2	38-	14	219	14	1	2	74	90	266
7	7	0	152	141	270	8	6	0	47	34	0	9	7	3	82	66	220	10	10	1	69-	35	12	12	1	3	139	141	182	14	2	0	86	66	0
7	7	1	199	196	45	8	6	1	119	117	326	9	8	0	50-	14	90	10	10	2	59	55	310	12	2	0	49-	63	0	14	2	1	51-	36	1
7	7	2	184	181	231	8	6	2	262	267	36	9	8	1	77-	59	289	10	10	3	3-	22	324	12	2	1	124	94	61	14	2	2	69	68	162
7	7	3	81	90	166	8	6	3	36-	29	312	9	8	2	113	104	142	10	11	0	44-	74	180	12	2	2	145	139	252	14	3	0	36-	12	0
7	7	4	36	30	90	8	6	4	101	103	184	9	8	3	97	102	103	10	11	1	132	115	354	12	2	3	73	70	279	14	3	1	105	90	319
7	8	0	40-	33	270	8	7	0	45-	15	0	9	9	0	50-	22	90	10	11	2	43	47	122	12	3	0	150	145	180	14	2	2	16-	59	307
7	8	1	332	298	319	8	7	1	87	75	116	9	9	1	76-	77	279	10	12	0	81	74	0	12	3	1	126	110	4	14	4	0	166	167	0
7	8	2	57	38	250	8	7	2	182	168	96	9	9	2	69	69	138	10	12	1	58-	48	259	12	3	2	37-	11	195	14	4	1	83	76	29
7	8	3	84	96	105	8	7	3	43	40	171	9	9	3	109	115	262	10	12	2	30	51	0	12	3	3	62	63	179	14	4	2	5-	55	144
7	8	4	15-	22	57	8	7	4	16-	5	349	9	10	0	141	133	90	10	13	0	36-	0	0	12	4	0	48-	23	180	14	5	0	23	19	0
7	9	0	102	103	90	8	8	0	62	53	180	9	10	1	125	102	227	10	13	1	104	104	15	12	4	1	71-	28	247	14	5	1	45-	31	340
7	9	1	62	74	12	8	8	1	186	175	198	9	10	2	66	59	1	10	13	2	12-	42	77	12	4	2	123	115	263	14	6	0	129	141	0
7	9	2	81	62	199	8	8	2	153	143	342	9	10	3	49	55	69	10	14	0	28-	6	180	12	4	3	15	24	215	14	6	1	51	44	92
7	9	3	65	72	125	8	8	3	44	45	186	9	11	0	48-	52	270	10	14	1	54	56	229	12	5	0	122	119	180	14	7	0	50	50	180
7	9	4	7-	12	236	8	9	0	142	149	0	9	11	1	71-	10	196	10	15	0	15-	62	0	12	5	1	162	135	255	14	7	1	61	65	42
7	10	0	193	168	90	8	9	1	172	153	102	9	11	2	48	42	118	11	0	1	162-	18	270	12	5	2	34-	3	270	14	8	0	85	119	0
7	10	1	243	222	302	8	9	2	112	106	90	9	11	3	46	55	192	11	0	2	112	112	180	12	5	3	10-	18	32	15	0	1	84	91	90
7	10	2	34	47	248	8	9	3	29-	18	199	9	12	0	45-	5	90	11	0	3	58	58	90	12	6	0	46-	41	0	15	1	0	27-	127	270
7	10	3	57	38	93	8	10	0	245	242	180	9	12	1	135	112	245	11	1	0	105	90	270	12	6	1	91	85	276	15	1	1	32-	29	171
7	11	0	265	264	90	8	10	1	75	72	129	9	12	2	51	52	356	11	1	1	162	139	311	12	6	2	60	59	233	15	2	0	24-	30	270
7	11	1	130	110	72	8	10	2	91	88	21	9	13	0	129	116	270	11	1	2	93	87	79	12	7	0	44-	61	0	15	2	1	82	109	49
7	11	2	37-	17	167	8	10	3	62	62	187	9	13	1	59-	35	154	11	1	3	37	26	247	12	7	1	64-	198	1	15	3	0	23-	50	270
7	11	3	70	67	146	8	11	0	47-	60	180	9	13	2	25-	26	212	11	2	0	201	193	90	12	7	2	29-	35	325	15	3	1	22-	45	89
7	12	0	28-	14	90	8	11	1	97	88	107	9	14	0	36-	6	270	11	2	1	77-	72	269	12	8	0	43-	14	0	15	4	0	21-	23	90
7	12	1	221	207	250	8	11	2	43	39	250	9	14	1	73	73	305	11	2	2	74	62	106	12	8	1	59-	41	301	15	5	0	11-	55	90
7	12	2	64	84	250	8	11	3	21	25	246																								

Table 5. *Bond lengths and angles*

S(1)–S(2)	2·075 (3) Å	C(4)–C(5)	1·369 (16) Å
S(1)–C(1)	1·744 (10)	C(5)–C(6)	1·391 (14)
S(2)–C(7)	1·742 (8)	C(6)–C(1)	1·386 (14)
C(1)–C(2)	1·408 (13)	C(6)–C(7)	1·449 (12)
C(2)–C(3)	1·385 (17)	C(7)–N	1·309 (11)
C(3)–C(4)	1·386 (21)	N–O	1·418 (10)
OH···N^{iii}	2·742 (11)		
C(1)–S(1)–S(2)	95·2 (0·3)°	C(6)–C(1)–C(2)	120·6 (0·9)°
S(1)–S(2)–C(7)	94·9 (0·3)	C(1)–C(2)–C(3)	118·4 (1·1)
S(1)–C(1)–C(6)	118·4 (0·6)	C(2)–C(3)–C(4)	120·2 (1·1)
S(2)–C(7)–C(6)	117·1 (0·6)	C(3)–C(4)–C(5)	121·4 (1·2)
C(1)–C(6)–C(7)	114·3 (0·7)	C(4)–C(5)–C(6)	119·4 (1·1)
C(7)–N–O	109·1 (0·7)	C(5)–C(6)–C(1)	119·8 (0·8)

This planarity is determined by the presence in the thiolinone ring of the trigonal carbon atoms, C(1), C(6) and C(7) as was shown in 4-methyl-1,2-dithio-4-cyclopentene-3-thione (Jeffrey & Shiono, 1959) in xanthane hydride (Stanford, 1963) and in thiuret hydrobromide (Foss & Tjomsland, 1958*a*) while in DL-6-thioctic acid (Karle, Estlin & Britts, 1967) and in 1,2-dithiolane-4-carboxylic acid (Foss & Tjomsland, 1958*b*) the presence of tetrahedral carbon atoms makes the dithiolane ring non planar.

The S–S distance is comparable to those generally found in other compounds (in non-cyclic compounds this distance is in the range 2·00–2·04 Å while in pentatomic rings the range is larger: 2·01–2·10 Å) and can

be considered to correspond to a pure single bond. The same can be said for the two C–S distances which are practically equal*. The N and O atoms of the oxime group are 0·07 and 0·06 Å respectively out of the dithiolic plane; this distortion is probably caused by the inner O···S(2) [2·663 (8) Å] contact which is considerably shorter than the sum of the van der Waals radii (3·0 Å) and does not correspond to an intramolecular hydrogen bond, since the oxygen atom is concerned in an intermolecular OH···N(iii) = 2·742 Å contact which is important in determining the packing. This last contact can justify the rather high (208–212 °C) melting point of the crystals. The C(7)–N [1·31 (1) Å] distance indicates a rather large double bond character for that bond, in agreement with the essentially single bond character of the distances C(7)–S(2) = 1·74 (1), C(7)–C(6) = 1·45 (1) and N–O = 1·42 (1) Å*. The C(7)–N and N–O distances and the angle C–N–O agree quite well with the corresponding values found in other oximes (Hamilton, 1961) particularly in formamidoxime (C–N = 1·288, N–O = 1·415 Å, C–N–O = 109·7°, Hall, 1965) in which the same prominent localization of the double bond is observed. This fact confirms the absence of a remarkable π delocalization in the dithiolic ring as indicated by the bond distances in it. The benzene ring is planar and its least-squares plane,

$$-0{\cdot}0098x + 0{\cdot}4864y + 0{\cdot}8735z = 0{\cdot}8663\,,$$

forms an angle of 177·8° with the thiolinone ring.

The packing, shown in the clinographic projection of Fig. 2, is mainly conditioned by the OH···N(iii) hydrogen bonds as already observed, which join the molecules in helical chains running along [001]. Other contacts shorter than 3·6 Å are as follows:

S(1)–S(1^{i}) = 3·59 Å	O–C(3^{v}) = 3·38 Å
S(1)–S(1^{iv}) = 3·59	O–N(ii) = 3·52
S(1)–S(2^{iv}) = 3·48	O–C(3^{vi}) = 3·50
S(2)–C(1^{ii}) = 3·53	N–C(5^{ii}) = 3·58

i $\frac{1}{2}-x,\bar{y},z+\frac{1}{2}$	iv $\frac{1}{2}-x,\bar{y},z-\frac{1}{2}$
ii $x,y,z+1$	v $\bar{x},y-\frac{1}{2},\frac{1}{2}-z$
iii $x-\frac{1}{2},y,z+\frac{1}{2}$	vi $x,y-\frac{1}{2},z-\frac{1}{2}$

* Taking into account the shortening of the bonds due to hybridization effects.

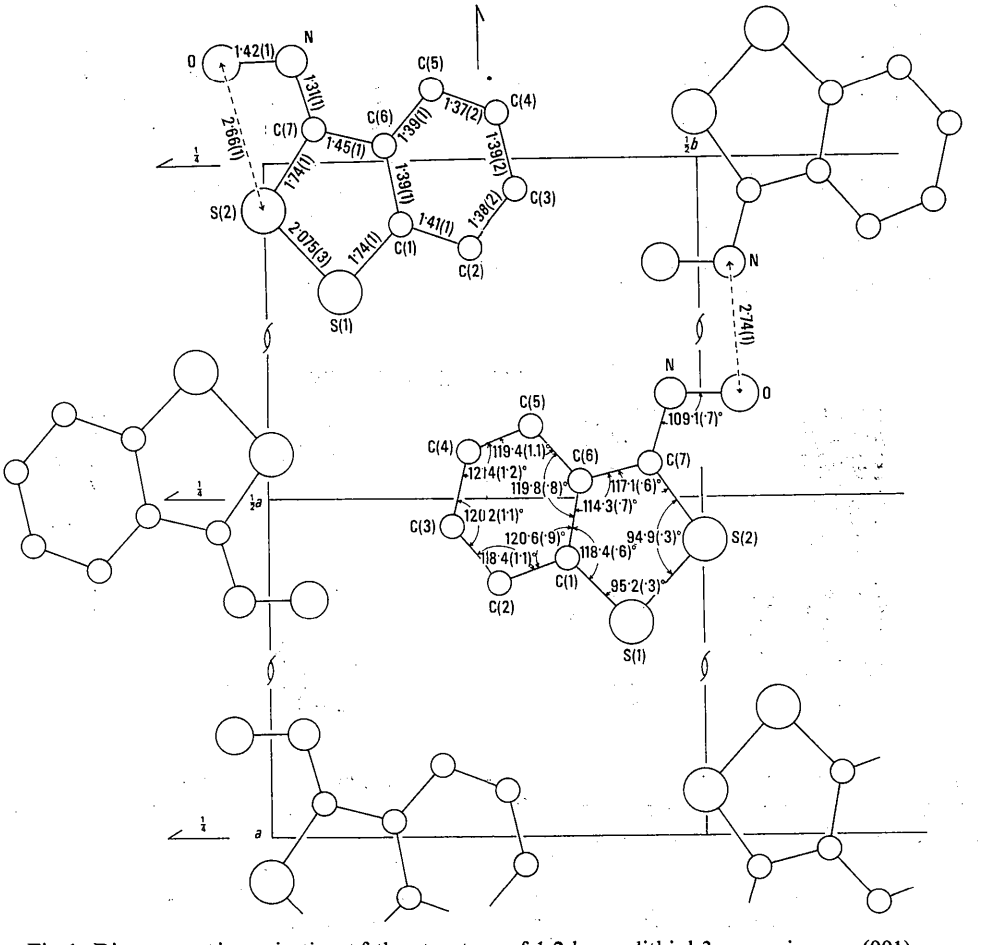


Fig. 1. Diagrammatic projection of the structure of 1,2-benzodithiol-3-one oxime on (001).

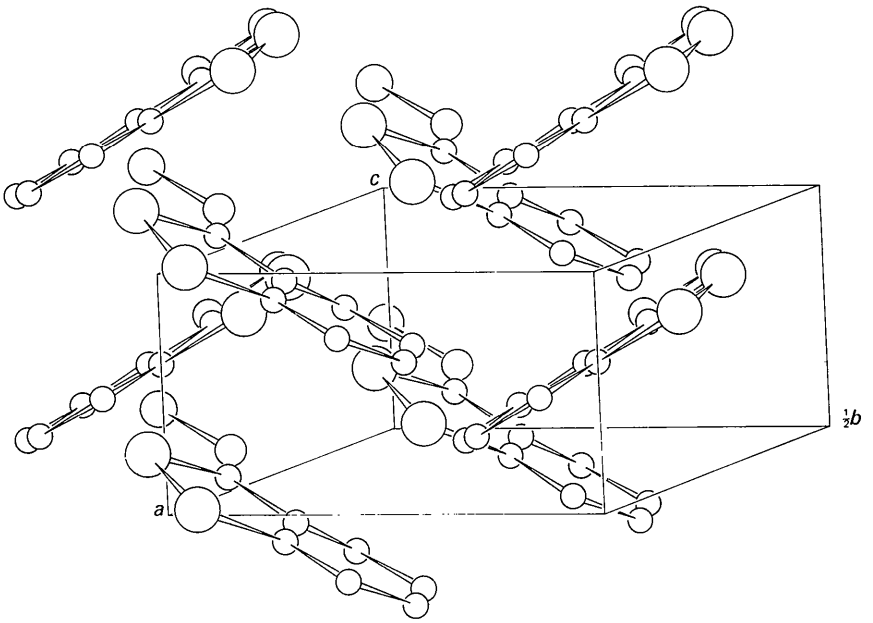


Fig. 2. Clinographic projection of the structure of 1,2-benzodithiol-3-one oxime.

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