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The Crystal and Molecular Structure of Tetrapyridine–Bis(diethylphosphorothioato) magnesium(II), a Model Substance For Polynucleotide Phosphorothioates

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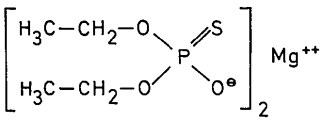
Tetrapyridine–bis(diethylphosphorothioato)magnesium(II) is monoclinic, space group $P2_1/c$, with $a=8{\cdot}691$, $b=9{\cdot}180$, $c=22{\cdot}000$ Å and $\beta=92{\cdot}51^\circ$, and calculated density 1·286 g cm^{-3}. The structure was solved by direct methods and refined by least squares with anisotropic thermal parameters to $R=4{\cdot}9\%$ for 2101 reflexions. Discrete molecules of the centrosymmetric complex show approximate octahedral coordination through pyridine nitrogen atoms and phosphorothioate oxygen atoms; sulphur atoms are not involved in coordination. The distances of 1·951 Å for P–S and 1·495 Å for P–O are consistent with an almost doubly bonded, nearly neutral sulphur atom and a singly bonded, negatively charged oxygen atom. This concept is reinforced by extended Hückel calculations on the diethylphosphorothioate ion, which give a bond overlap population for P–S twice that for P–O and Mulliken charges more negative for O than S. The implications of this study for the understanding of the biochemical behaviour of polynucleotide phosphorothioates are discussed.

Introduction

Nucleoside phosphorothioates are of increasing biochemical interest. As the monomer they serve sometimes as substrates and sometimes as inhibitors for the enzymes of nuclei acid metabolism (Eckstein, 1970; Murray & Atkinson, 1968; Hampton, Brox & Bayer, 1969). As double-stranded polymers they may stimulate the production of interferon against virus infection, in some cases even more effectively than the corresponding polynucleotides (DeClercq, Eckstein & Merigan, 1969; DeClercq, Eckstein, Sternbach & Merigan, 1970), possibly because they are catabolized more slowly. Because divalent metal ions are so often necessary for activity of the enzymes concerned and play such an important part in stabilizing a polynucleotide conformation, we have investigated magnesium bis-(diethylphosphorothioate), as a model system for the interaction of divalent metal ions with phosphorothioate diesters.



In a single-crystal X-ray diffraction study we sought to establish whether the magnesium ion is complexed *via* oxygen, sulphur, or both, and how strongly, and what conformation of the diester is preferred.

Experimental

Tetrapyridine-bis(diethylphosphorothioato)magnesium-(II) crystallized from pyridine at room temperature on addition of light petroleum (40–60°) as light-yellow stout prisms. The monoclinic symmetry and the extinctions of $h0l$ reflexions with l odd and $0k0$ reflexions with k odd indicated the space group $P2_1/c$. Unit-cell dimensions based on 4-circle diffractometer measurements obtained with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0{\cdot}70926$ Å) at 22 (2)°C and refined by least-squares are $a=8{\cdot}691$ (3), $b=9{\cdot}180$ (3), $c=22{\cdot}000$ (8) Å and $\beta=92{\cdot}51$ (5)°, where estimated standard deviations are enclosed in parentheses. Two formula units of the complex ($MgS_2P_2O_6N_4C_{28}H_{40}$, F.W. 679·02) occupy the unit cell, one half per asymmetric unit, with magnesium ions at centres of symmetry. This composition yields $F(000)=716$ electrons and density $\varrho_{calc}=1{\cdot}286$ g cm^{-3}. Solubility in flotation media precluded an accurate density measurement, but the presence in the final difference electron density synthesis of no peak higher than 0·25 eÅ^{-3} except in the vicinity of third-row atoms indicates the correctness of this formulation.

A crystal of dimensions $0{\cdot}15\times0{\cdot}20\times0{\cdot}30$ mm was sealed in a capillary to prevent loss of pyridine during data collection. With a linear absorption coefficient $\mu=0{\cdot}304$ mm^{-1} for Mo $K\alpha$ radiation the correction to F for absorption along a straight path through the crystal ranged from a minimum of 1·021 to a maximum of 1·057; this variation in absorption was neglected.

Intensity data for 2291 reflexions were collected on a Stoe automated four-circle diffractometer by the θ–2θ scan method with stationary background counts before and after the scan. Data were corrected for geometrical factors and later for extinction *via* a plot of I_c/I_o *versus* I_c. Standard errors σ were assigned considering counting statistics as well as 3% of intensity allowance for other error sources (Stout & Jensen, 1968); 190 reflexions with $F<3\sigma_F$ were not used in

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Table 1. *Observed and calculated structure factors (multiplied by 10)*

H	K	L	FOBS	FCAL
0	0	2	719	727
0	0	4	855	-858
0	0	6	719	710
0	0	8	74	85
0	0	10	64	-82
0	0	12	961	-959
0	0	14	528	519
0	0	16	157	161
0	0	18	282	-259
0	0	20	98	96
0	0	22	111	-109
0	1	1	871	867
0	1	2	750	-755
0	1	3	123	113
0	1	4	548	556
0	1	5	760	766
0	1	6	180	172
0	1	7	655	-627
0	1	8	501	497
0	1	9	247	239
0	1	10	177	168
0	1	11	221	220
0	1	12	91	85
0	1	13	151	139
0	1	14	136	130
0	1	15	312	295
0	1	16	407	-408
0	1	17	184	-197
0	1	18	76	-78
0	1	19	59	65
0	1	20	60	52
0	1	21	87	77
0	1	22	28	17
0	2	0	536	-571
0	2	1	821	-811
0	2	2	651	-638
0	2	3	565	-585
0	2	4	164	168
0	2	5	381	369
0	2	6	99	90
0	2	7	119	-119
0	2	8	55	52
0	2	9	90	80
0	2	10	124	121
0	2	11	165	171
0	2	12	518	518
0	2	13	270	270
0	2	14	104	107
0	2	15	473	-471
0	2	16	69	59
0	2	17	162	-169
0	2	18	275	268
0	2	19	239	197
0	2	20	84	85
0	2	21	170	-110
0	2	22	73	41
0	3	1	805	-880
0	3	2	709	-721
0	3	3	335	332
0	3	4	10	7
0	3	5	175	155
0	3	6	432	390
0	3	7	255	-262
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0	3	9	609	600
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0	3	11	77	77
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0	3	13	170	169
0	3	14	271	-277
0	3	15	275	-240
0	3	16	47	-67
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0	3	18	72	-47
0	3	19	76	-66
0	3	20	38	36
0	4	0	612	-618
0	4	1	224	245
0	4	2	192	200
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0	4	4	264	249
0	4	5	160	161
0	4	6	107	-98
0	4	7	272	281
0	4	8	197	188
0	4	9	167	-162
0	4	10	94	95
0	4	11	139	111
0	4	12	68	79
0	4	13	235	-197
0	4	14	158	-184
0	4	15	117	118
0	4	16	63	67
0	4	17	162	170
0	4	18	216	218
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0	5	0	532	570
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0	5	3	177	189
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0	5	5	181	-175
0	5	6	242	-248
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0	5	11	51	30
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0	5	14	166	181
0	5	15	136	134
0	5	16	297	298
0	5	17	72	70
0	5	18	47	-27
0	5	19	130	134
0	6	0	83	84
0	6	1	129	131
0	6	2	27	-22
0	6	3	50	57
0	6	4	188	186
0	6	5	75	-70
0	6	6	216	229
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0	6	8	58	57
0	6	9	42	41
0	6	10	124	-138
0	6	11	111	-118
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0	6	13	77	81
0	6	14	180	-178
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0	7	2	69	62
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0	7	8	113	117
0	7	9	138	130
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0	8	1	238	-237
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1	1	14	170	-169
1	1	15	681	-691
1	1	16	179	-180
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1	1	20	58	63
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1	2	8	69	69
1	2	9	153	148
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4	1	7	655	-627
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4	3	17	271	276
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4	4	2	192	200
4	4	3	268	-278
4	4	4	264	249
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4	4	6	107	-98
4	4	7	272	281
4	4	8	197	188
4	4	9	167	-162
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4	4	11	139	111
4	4	12	68	79
4	4	13	235	-197
4	4	14	158	-184
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4	4	18	216	218
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4	5	4	47	-45
4	5	5	181	-175
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Table 1 (*cont.*)

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1	6	5	92	82
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1	6	7	96	-93
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1	6	9	80	72
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1	6	12	187	-144
1	6	13	116	-106
1	6	14	95	-90
1	6	15	21	14
1	6	16	61	-6
1	6	17	80	80
1	6	18	21	0
1	7	-11	207	210
1	7	-10	170	-167
1	7	-9	69	-98
1	7	-8	131	135
1	7	-7	25	7
1	7	-6	268	256
1	7	-5	113	110
1	7	-4	116	-142
1	7	-3	61	81
1	7	-2	317	318
1	7	-1	271	-291
1	7	0	47	-40
1	7	2	124	-110
1	7	3	77	-74
1	7	4	61	-67
1	7	5	137	-133
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1	7	10	76	-74
1	7	11	57	-49
1	7	12	65	-48
1	7	13	111	111
1	7	14	123	-112
1	7	15	240	-255
1	7	16	651	651
1	7	17	472	435
1	7	18	335	-337
1	8	-11	890	897
1	8	-10	64	67
1	8	-9	12	11
1	8	-8	15	10
1	8	-7	293	295
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1	8	-5	150	-162
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2	3	15	137	-133
2	4	15	47	-48
2	5	15	98	-98
2	6	15	124	-98
2	7	15	81	71
2	8	15	76	-74
2	9	15	57	-49
2	10	15	65	-48
2	11	15	111	111
2	12	15	123	-112
2	13	15	240	-255
2	14	15	651	651
2	15	15	472	435
2	16	15	335	-337
2	17	15	890	897
2	18	15	64	67
2	-21	16	134	111
2	-20	16	85	-90
2	-19	16	187	-144
2	-18	16	116	-106
2	-17	16	95	-90
2	-16	16	21	14
2	-15	16	61	-6
2	-14	16	80	80
2	-13	16	21	0
2	-12	16	207	210
2	-11	16	170	-167
2	-10	16	69	-98
2	-9	16	131	135
2	-8	16	25	7
2	-7	16	268	256
2	-6	16	113	110
2	-5	16	116	-142
2	-4	16	61	81
2	-3	16	317	318
2	-2	16	271	-291
2	-1	16	47	-40
2	0	16	124	-110
2	1	16	77	-74
2	2	16	61	-67
2	3	16	137	-133
2	4	16	47	-48
2	5	16	98	-98
2	6	16	124	-98
2	7	16	81	71
2	8	16	76	-74
2	9	16	57	-49
2	10	16	65	-48
2	11	16	111	111
2	12	16	123	-112
2	13	16	240	-255
2	14	16	651	651
2	15	16	472	435
2	16	16	335	-337
2	17	16	890	897
2	18	16	64	67
2	-21	17	111	111
2	-20	17	85	-90
2	-19	17	187	-144
2	-18	17	116	-106
2	-17	17	95	-90
2	-16	17	21	14
2	-15	17	61	-6
2	-14	17	80	80
2	-13	17	21	0
2	-12	17	207	210
2	-11	17	170	-167
2	-10	17	69	-98
2	-9	17	131	135
2	-8	17	25	7
2	-7	17	268	256
2	-6	17	113	110
2	-5	17	116	-142
2	-4	17	61	81
2	-3	17	317	318
2	-2	17	271	-291
2	-1	17	47	-40
2	0	17	124	-110
2	1	17	77	-74
2	2	17	61	-67
2	3	17	137	-133
2	4	17	47	-48
2	5	17	98	-98
2	6	17	124	-98
2	7	17	81	71
2	8	17	76	-74
2	9	17	57	-49
2	10	17	65	-48
2	11	17	111	111
2	12	17	123	-112
2	13	17	240	-255
2	14	17	651	651
2	15	17	472	435
2	16	17	335	-337
2	17	17	890	897
2	18	17	64	67
2	-21	18	111	111
2	-20	18	85	-90
2	-19	18	187	-144
2	-18	18	116	-106
2	-17	18	95	-90
2	-16	18	21	14
2	-15	18	61	-6
2	-14	18	80	80
2	-13	18	21	0
2	-12	18	207	210
2	-11	18	170	-167
2	-10	18	69	-98
2	-9	18	131	135
2	-8	18	25	7
2	-7	18	268	256
2	-6	18	113	110
2	-5	18	116	-142
2	-4	18	61	81
2	-3	18	317	318
2	-2	18	271	-291
2	-1	18	47	-40
2	0	18	124	-110
2	1	18	77	-74
2	2	18	61	-67
2	3	18	137	-133
2	4	18	47	-48
2	5	18	98	-98
2	6	18	124	-98
2	7	18	81	71
2	8	18	76	-74
2	9	18	57	-49
2	10	18	65	-48
2	11	18	111	111
2	12	18	123	-112
2	13	18	240	-255
2	14	18	651	651
2	15	18	472	435
2	16	18	335	-337
2	17	18	890	897
2	18	18	64	67
3	6	-7	155	-161
3	6	-6	408	480
3	6	-5	76	-84
3	6	-4	127	146
3	6	-3	96	-96
3	6	-1	112	-99
3	6	0	61	53
3	6	1	159	-155
3	6	2	119	133
3	6	3	123	127
3	6	5	92	82
3	6	6	259	-255
3	6	7	96	-93
3	6	8	210	210
3	6	9	80	72
3	6	10	134	111
3	6	11	85	-90
3	6	12	187	-144
3	6	13	116	-106
3	6	14	95	-90
3	6	15	21	14
3	6	16	61	-6
3	6	17	80	80
3	6	18

refinement. From the equation $E_{\mathbf{h}}=(F_h^2/\langle F^2\rangle)^{1/2}$, where $\langle F^2\rangle$ is a local average over $\frac{1}{20}$ the range of sin θ, normalized structure factors (Karle & Karle, 1966; Hall, 1968) were calculated. With the signs of three reflexions fixed to specify the origin, and of two more permuted, tangent formula extension (Karle & Karle, 1966; Hall, 1968) developed phases for 215 reflexions with $E>1{\cdot}5$, all correctly. The preponderance of positive signs (153 *versus* 62 negative) suggested the presence of the magnesium ion at the origin. An E map was calculated, third-row atoms were located, and a Fourier synthesis based on structure factors phased with these atoms revealed all other non-hydrogen atoms. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) of coordinates and thermal parameters (first isotropic, then anisotropic) reduced $R[=\sum||F_{obs}|-|F_{calc}||/\sum|F_{obs}|]$ to 7·6% by minimizing $\sum 1/\sigma 2(|F_{obs}|-1/K|F_{calc}|)^2$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1965). At this point the hydrogen atoms could be clearly seen in a difference map, where at heights up to 0·75 e Å^{-3} all but one of them exceeded the highest background peak of 0·25 e Å^{-3}. Further refinement of non-hydrogen atomic parameters, with hydrogen coordinates fixed and hydrogen thermal parameters fixed at those of the attached atoms, led to a final R of 4·9% for 2101 reflexions (Table 1) with average parameter shifts, in the final cycle, less than $\frac{1}{3}$ the e.s.d.

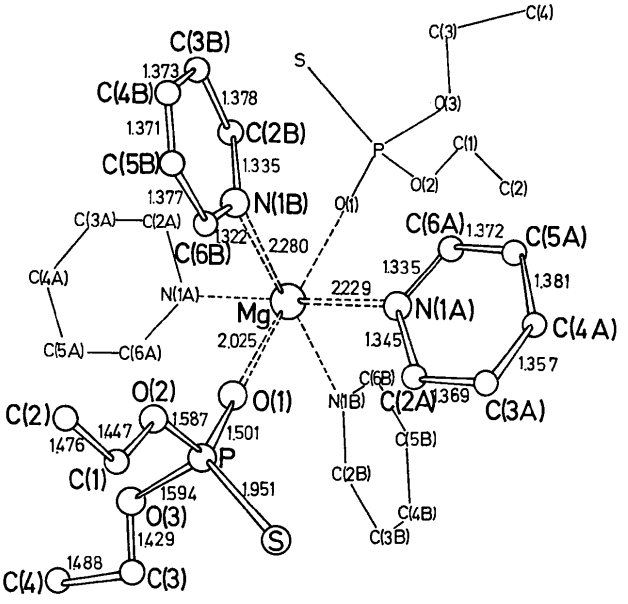

Fig. 1. The complex viewed along the approximate threefold axis of the coordination polyhedron, with bond distances.

Positional and thermal parameters for atoms refined anisotropically are given in Table 2, and hydrogen-atom coordinates and distances in Table 3. Figs. 1 and 2 depict the molecule, respectively viewed along the approximate threefold axis of the coordination polyhedron with bond distances drawn in, and viewed along **a** with bond angles indicated. Standard deviations based on the variance–covariance matrix from refinement are: 0·001 Å for distances between third-row atoms, 0·002 Å between third- and second-row atoms, and 0·004 to 0·006 Å between two second-row atoms; corresponding bond angles show standard deviations of 0·1, 0·1 and 0·3° respectively. Carbon–hydrogen distances have estimated error 0·15–0·20 Å.

Table 2. *Fractional atomic coordinates and anisotropic thermal parameters in the form* $T=exp\ -(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{12}hl+2\beta_{23}kl)$

All values are $\times 10^4$.

Estimated standard deviations are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg	0 (0)	0 (0)	0 (0)	91 (2)	77 (2)	12 (1)	− 1 (2)	−1 (1)	−1 (1)
P	− 996 (1)	1562 (1)	1392 (1)	114 (1)	85 (1)	12 (1)	5 (1)	2 (1)	−2 (1)
S	652 (1)	1647 (1)	2022 (1)	155 (2)	144 (1)	15 (1)	5 (1)	− 9 (1)	−5 (1)
O(1)	− 642 (2)	910 (2)	791 (1)	117 (3)	95 (3)	14 (1)	6 (3)	2 (1)	−6 (1)
O(2)	−1693 (3)	3117 (2)	1229 (1)	171 (4)	90 (3)	16 (1)	26 (3)	−1 (1)	−3 (1)
O(3)	−2495 (3)	811 (3)	1640 (1)	141 (4)	130 (3)	21 (1)	− 6 (3)	7 (1)	9 (1)
N(1*A*)	2307 (3)	1060 (3)	120 (1)	110 (4)	94 (4)	16 (1)	− 3 (3)	−0 (1)	−3 (1)
C(2*A*)	2919 (4)	1386 (4)	674 (1)	112 (5)	156 (6)	19 (1)	− 8 (4)	0 (2)	−10 (2)
C(3*A*)	4341 (4)	1990 (5)	766 (2)	122 (6)	197 (7)	25 (1)	−27 (5)	−9 (2)	−13 (2)
C(4*A*)	5208 (4)	2283 (5)	283 (2)	117 (6)	188 (7)	33 (1)	−43 (5)	−1 (2)	−6 (2)
C(5*A*)	4611 (5)	1963 (5)	− 288 (2)	149 (6)	184 (7)	26 (1)	−46 (5)	15 (2)	0 (2)
C(6*A*)	3174 (4)	1354 (4)	− 346 (2)	148 (6)	140 (6)	18 (1)	−32 (5)	2 (2)	−2 (2)
N(1*B*)	− 872 (3)	1984 (3)	− 538 (1)	111 (4)	92 (4)	15 (1)	1 (3)	0 (1)	−0 (1)
C(2*B*)	−1157 (4)	1965 (4)	−1138 (2)	186 (7)	125 (5)	16 (1)	30 (5)	3 (2)	−2 (2)
C(3*B*)	−1656 (5)	3161 (5)	−1468 (2)	284 (9)	150 (6)	16 (1)	56 (6)	−2 (2)	8 (2)
C(4*B*)	−1894 (5)	4443 (4)	−1170 (2)	252 (8)	117 (6)	25 (1)	35 (5)	2 (2)	15 (2)
C(5*B*)	−1633 (5)	4483 (4)	− 554 (2)	196 (7)	96 (5)	22 (1)	7 (5)	1 (2)	2 (2)
C(6*B*)	−1119 (4)	3244 (4)	− 260 (1)	143 (5)	104 (5)	16 (1)	−10 (4)	4 (2)	1 (2)
C(1)	−2130 (5)	4107 (4)	1702 (2)	277 (9)	110 (5)	24 (1)	43 (6)	0 (2)	−17 (2)
C(2)	−2823 (6)	5406 (5)	1418 (2)	350 (12)	124 (6)	43 (2)	86 (7)	−16 (3)	−19 (2)
C(3)	−2436 (5)	− 421 (4)	2036 (2)	230 (8)	142 (6)	20 (1)	−46 (5)	10 (2)	8 (2)
C(4)	−4010 (6)	− 725 (6)	2233 (2)	278 (11)	277 (10)	44 (2)	−70 (8)	40 (3)	28 (3)

Table 3. *Hydrogen atom fractional coordinates* ($\times 10^{-3}$) *and distances to attached heavy atoms with estimated standard deviations*

	x	*y*	*z*	Distance
H(2*A*)	215 (10)	127 (9)	101 (4)	1·02 (15) Å
H(3*A*)	474 (10)	226 (9)	119 (4)	1·00 (15)
H(4*A*)	623 (10)	270 (9)	35 (4)	0·98 (15)
H(5*A*)	524 (10)	205 (9)	− 64 (4)	0·97 (15)
H(6*A*)	285 (10)	107 (9)	− 75 (4)	0·95 (15)
H(2*B*)	− 96 (10)	113 (9)	−135 (4)	0·91 (15)
H(3*B*)	−168 (10)	312 (9)	−184 (4)	0·82 (15)
H(4*B*)	−208 (10)	527 (9)	−139 (4)	0·91 (15)
H(5*B*)	−189 (10)	543 (9)	− 28 (4)	1·09 (15)
H(6*B*)	−104 (10)	325 (9)	19 (4)	0·99 (15)
H(11)	−137 (13)	432 (12)	197 (5)	0·9 (2)
H(12)	−298 (13)	336 (12)	198 (5)	1·2 (2)
H(21)	−318 (13)	605 (12)	184 (5)	1·2 (2)
H(22)	−215 (13)	615 (12)	119 (5)	1·0 (2)
H(23)	−341 (13)	525 (12)	110 (5)	0·9 (2)
H(31)	−200 (13)	−144 (12)	178 (5)	1·2 (2)
H(32)	−177 (13)	− 28 (12)	238 (5)	0·9 (2)
H(41)	−441 (13)	13 (12)	247 (5)	1·0 (2)
H(42)	−464 (13)	− 85 (12)	192 (5)	0·9 (2)
H(43)	−397 (13)	−142 (12)	250 (5)	0·9 (2)

Results and discussion

Coordination at magnesium

The $M(A^-)_2(py)_4$ stoichiometry of this complex is of a type frequently found in the Schaeffer complexes of transition metals (Schaeffer, Dorsey, Skinner & Christian, 1957). The centrosymmetric coordination polyhedron around magnesium has approximate octahedral and almost exact D_{2h} symmetry. Magnesium–ligand vectors deviate from perpendicularity by at most 1·1°. The Mg–O distance of 2·031 (2) Å is fairly short and suggests a strong interaction: it compares with aquo complex values of 2·074 Å in magnesium citrate decahydrate (Johnson, 1965), 2·099 Å in aquomagnesium tetraphenylporphyrin (MgTPP) (Timkovich & Tulinsky, 1969) and 2·15 Å in $Mg(H_2O)_2$ (acetylacetonate)$_2$ (Morosin, 1967), with etherate complex values of 2·01 and 2·06 Å in $C_6H_5MgBr(C_4H_{10}O)_2$ (Stucky & Rundle, 1964), 2·03 and 2·06 Å in $C_2H_5MgBr(C_4H_{10}O)_2$ (Guggenberger & Rundle, 1964), 2·10 Å in $MgBr_2$

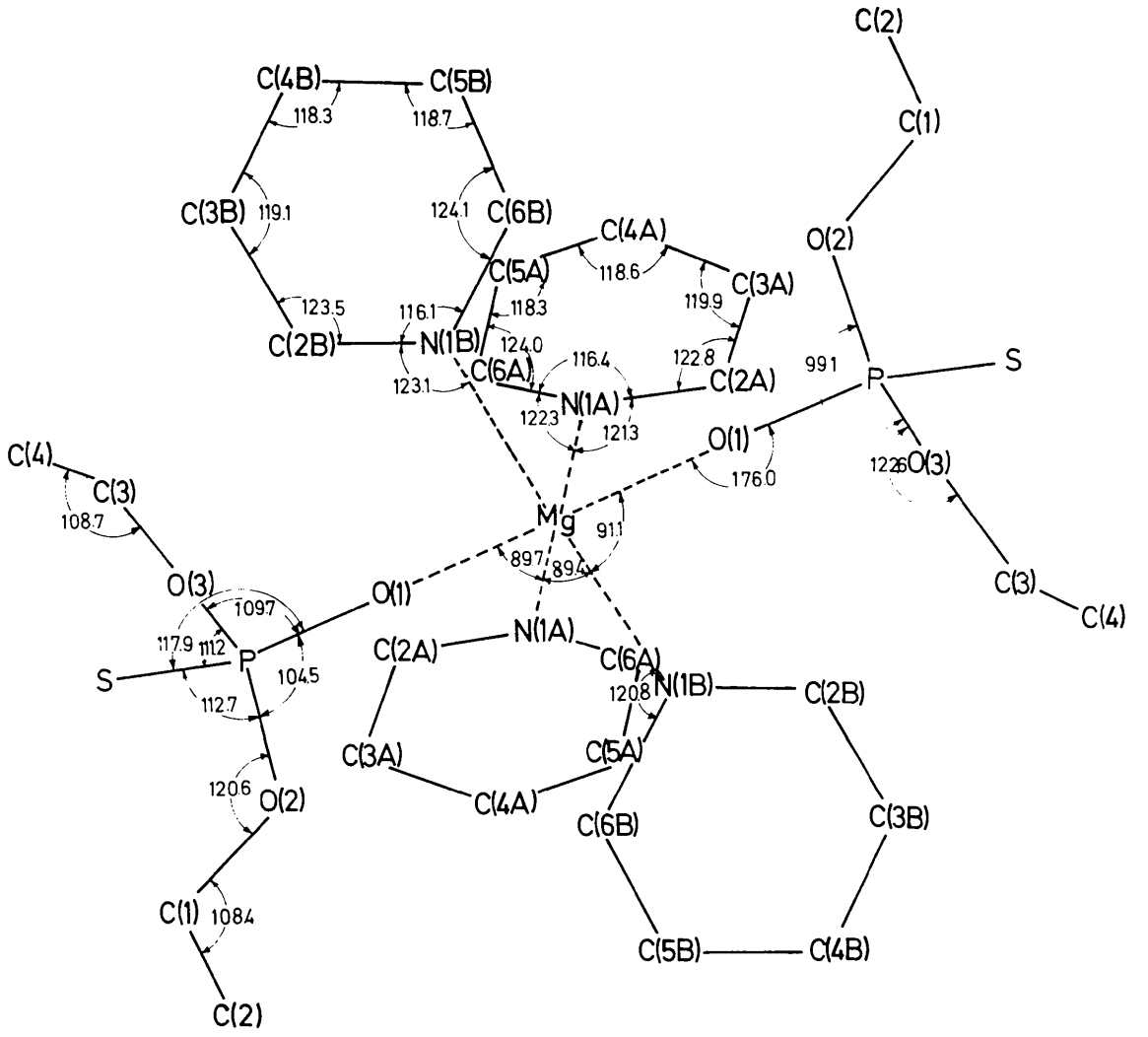

Fig. 2. The complex viewed along **a**, with bond angles.

(tetrahydrofuran)$_4$ (Perucaud & Le Bihan, 1968), and 2·09 to 2·16 Å in $MgBr_2(C_4H_{10}O)_2$ (Schibilla & Le Bihan, 1967), and with keto complex distances of 2·03 and 2·04 Å (Morosin, 1967) and 2·019, 2·031, 2·072, 2·077, 2·081 and 2·118 (Johnson, 1965). The long and variable Mg–N distances of 2·234 (3) and 2·283 (3) Å suggest a weaker interaction; in the amine complex $[C_2H_5MgBr(C_2H_5)_3N]_2$ (Toney & Stucky, 1967) the distance is only 2·15 Å, while in the chelate MgTPP (Timkovich & Tulinsky, 1969) it is even shorter at 2·072 Å. The interaction of the magnesium with the phosphorothioate ion appears to dominate that with pyridine; thus the complexing *via* phosphorothioate oxygen is probably a general phenomenon not restricted to this case.

The pyridine ligands

Pyridine rings are strictly planar: no non-hydrogen atom in either ring deviates by more than 0·006 Å from the least-squares plane. Bond distances may be compared with values found by microwave spectroscopy on pyridine vapour (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) of 1·3402 Å for N(1)–C(2) and N(1)–C(6), 1·3944 Å for C(2)–C(3) and C(5)–C(6), and 1·3945 Å for C(3)–C(4) and C(4)–C(5). The correspondence of bond angles is particularly noteworthy: in the vapour (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) the neighbouring ring atoms subtend angles of 116·83° at N(1), 123·88° at C(2) and C(6), 118·53° at C(3) and C(5), and 118·33° at C(4), and no ring angle in Fig. 2 differs by more than 1·4° from these values, while the average deviation is only 0·5°. Ring planes *A* and *B* are nearly orthogonal, intersecting at an angle of 82·7°. They miss the Mg ion by 0·07 and 0·03 Å respectively. The dihedral angles C(2*A*, 6*B*)–N(1*A*, 1*B*)–Mg–O(1) are only 18 and 27°, showing a tendency for the rings to lie in the same plane as the Mg–O(1) bond. Van der Waals contacts of 2·6 (2) Å, the standard value (Pauling, 1960), occurring between H(6*A*) and O(1), H(6*A*) and O(3), and H(2*B*) and O(1), restrict the alignment, as does the short H(2*B*)–S distance of 3·0 (2) Å (3·05 Å expected, Pauling, 1960). Although the pyridine rings do not interfere intramolecularly [even the nitrogen atoms have adequate separation with N(1*A*)–N(1*B*)=3·212 (4) Å], their intermolecular interactions dominate the packing scheme in two directions, as shown in Fig. 3. Interference of C(6*B*) and H(6*B*) with H(4*A*) of the molecule translated one unit-cell along **a** prevents closer approach in that direction. The *A* rings are still able to stack, but at a vertical separation of 3·6 Å the π–π interactions are unlikely to be significant. In a similar manner the *B* rings of adjacent complexes translated along **b** pack parallel, but only hydrogen atoms overlap and the perpendicular distance between rings is 2·5 Å.

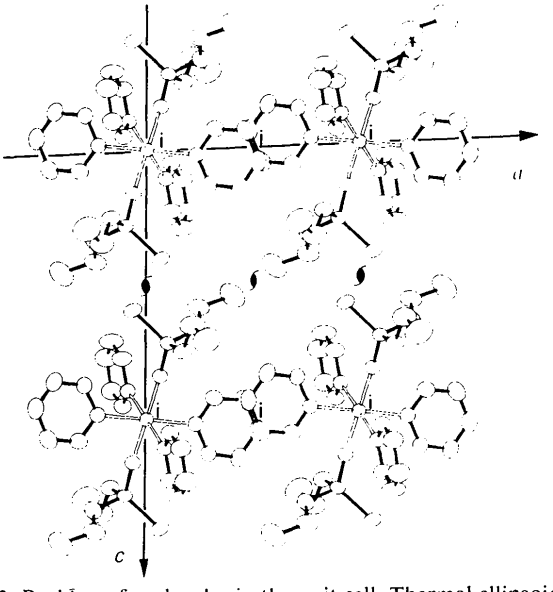

Fig. 3. Packing of molecules in the unit cell. Thermal ellipsoids correspond to 50% probability.

The diethylphosphorothioate anion

The geometry of the phosphorus coordination shows the expected pattern: S–P–O angles greater than O–P–O because of the bulk of the sulphur atom, but all angles within 10° of tetrahedral. The P–S distance of 1·951 (1) Å agrees well with the 1·946 Å observed in uridine-2′,3′-*O*,*O*-cyclophosphorothioate (UPS) (Saenger & Eckstein, 1970) and is shorter than the majorityof the one-and-a-half bond distances observed in the *O*,*O*′-diethylphosphorothioate complexes (Ito, Igarashi & Hagihara, 1969; McConnell & Kastalsky, 1967; Fernando & Green, 1967; Ooi & Fernando, 1967; Ito, 1972; Furlani, Tomlinson, Porta & Sgamellotti, 1970; Knox & Prout, 1969; Lawton & Kokotailo, 1969; Lawton, 1971; Coppens, MacGillavry, Hovenkamp & Douwes, 1962; Kastalsky & McConnell, 1969; Shetty & Fernando, 1970) listed in Table 4, where the range is 1·913–2·024 Å and the unweighted average 1·974 Å with standard deviation 0·022 Å. The P–O(R) bonds at 1·586 (2) and 1·591 (2) Å agree exactly with the literature value (Corbridge, 1966) of 1·59 (5) Å. The P–O(Mg) bond at 1·495 (2) Å may be compared with 1·48 Å in UPS (Saenger & Eckstein, 1970), and lies between average values (Corbridge, 1966) of 1·48 (4) Å for structures formally written P → O and 1·51 (2) Å for a formal P–O$^-$.

Thus the nature of the P–O bond is not clear from the bond distance alone; consequently quantum-mechanical calculations (see below) were undertaken.

The P–O–C and O–C–C angles approach trigonal and tetrahedral values respectively, as is the case in barium diethylphosphate (Kyogoku & Iitaka, 1966) and nearly all diethylphosphorodithioate complexes studied. Although the ethyl C–C bond distances seem surprisingly short, a similar effect appears in nearly all analyses (Kyogoku & Iitaka, 1966; Ito, Igarashi & Hagihara, 1969; McConnell & Kastalsky, 1967; Fernando & Green, 1967; Ooi & Fernando, 1967; Ito, 1972; Furlani, Tomlinson, Porta & Sgamellotti, 1970;

Knox & Prout, 1969), where the range is 1·26 to 1·54 Å, average 1·43 Å, and standard deviation 0·09 Å. Some of these values were undoubtedly affected by libration. In the present case thermal motion of ethyl carbon atoms is moderate: the r.m.s. components along principal axes range from 0·18 to 0·40 Å.

Of great significance are the dihedral angles in the C–C–O–P–O–C–C chain. Relevant dihedral angles in S-substituted phosphodiesters and in polynucleotides (Table 4) show striking trends. The S–P–O–C arrangement is *gauche* (60°) in the great majority of reported cases. The *gauche* (60°) arrangement of the P–S bond to both O–C bonds is not obvious *a priori* in view of the bulk of the sulphur atom; the small magnitude of the dihedral angle, even less than 60° in this and several other studies, is very surprising. In the polynucleotide structures (Arnott, Dover & Wonacott, 1969; Arnott, 1970) A-DNA, B-DNA, α-RNA and β-RNA no unesterified oxygen atom is in a position where the corresponding P–O bond is *gauche* (60°) to both ester O–C bonds (Table 4); however, this does occur for O(3) in C-DNA (Marvin, Spencer, Wilkins & Hamilton, 1961) (Table 4). Only in the C-DNA conformation with S replacing O(3) can a phosphorothioate polynucleotide preserve the usual monomer geometry.

The P–O–C–C dihedral angle is generally *trans* in the ethyl series (Ito, Igarashi & Hagihara, 1969; McConnell & Kastalsky, 1967; Fernando & Green, 1967;

Table 4. *Dihedral angles*[a] *in phosphodiester structures*

Complex	Ref.	∠S–P–O–C[b]	∠O–P–O–C[b]	∠P–O–C–C[b]
$Mg[(EtO)_2)_2POS]_2.(NC_5H_5)$	This work	48; 39	178[c] 69; 93[c], 158	176; 173
$Ba[(EtO)_2PO_2]_2$	1		173[c], 72; 175[c], 68	174; 177
$(C_6H_5CH_2)_2POOH$	2		173[c], 67; 73[c], 172	176; 176
$Zn[(EtO)_2PS_2]_2$	3	56, 66; 70, 53; 39, 88; 55, 69	176; 171; 154; 172	179; 179;166; 133
$Ni[(EtO)_2PS_2]_2$	4	61, 56; 52, 68	178; 172	178; 164
$Ni[(EtO)_2PS_2]_2$	5	67, 54; 54, 67	175; 171	178; 160
$Ni[(EtO)_2PS_2]_2.(NC_5H_5)_2$	6	60, 67; 67, 59	173; 176	177; 179
$Pb[(EtO)_2PS_2]_2$	7	45, 172; 66, 64; 52, 180; 178, 55	71; 178; 59; 60	118; 179; 131; 173
$V[(EtO)_2PS_2]_3$	8	70, 54; 66, 58; 44, 80	172; 175; 162	177; 175; 166
$Mo_2O_3[(EtO)_2PS_2]_4.(C_6H_4Cl_2)_2$	9	129, 6; 60, 66; 60, 60; 54, 67	119; 172; 178; 175	159; 178; 146; 174
$Zn[(i\text{-}PrO)_2PS_2]_2$	10	81, 43; 46, 80; 22, 150; 85, 44	161; 164; 96, 155	110, 134; 107, 145; 97, 167; 179, 89
$Cd[(i\text{-}PrO)_2PS_2]_2$	10	96, 30; 36, 92; 24, 152; 55, 75	146; 151; 85; 174	112, 150; 114, 161; 99, 168; 156, 120
$Hg[(i\text{-}PrO)_2PS_2]_2$	11	65, 61; 84, 44; 56, 66; 78, 48	177; 166; 172; 168	128, 117; 121, 131; 148, 101; 124, 118
$K(MeO)_2PS_2$	12	17, 152	88	
$Ni[(MeO)_2PS_2]_2$	13	62, 56; 59, 59	177; 180	
$Ni[(MeO)_2PS_2]_2.N_2H_8C_{12}$	14	162, 39; 70, 56; 178, 54; 62, 64	79; 175; 66; 176	
$Ni[(MeO)_2PS_2]_2.N_2H_{12}C_{12}$	14	49, 172; 78, 49; 154, 26; 164, 36	69; 164; 98; 88	
α-RNA (11-fold helix)	15		177[cd], 49[cd], 67[d]; 49[ce], 178[ce], 66[e]	85[d], 158[d]; 174[e]
β-RNA (11-fold helix)	15		177[cd], 49[cd], 67[d]; 50[ce], 66[e]	85[d], 158[d]; 174[e]
A-DNA	15		179[cd], 53[cd], 63[d]; 47[ce], 176[ce], 69[e]	83[d], 160[d]; 168[e]
B-DNA	15		141[cd], 15[cd], 104[d]; 67[ce], 152[ce], 40[e]	55[d], 170[d]; 164[e]
C-DNA	16		35[cd], 94[cd], 148[d]; 159[ce], 72[ce], 45[e]	99[d], 149[d]; 143[e]
Uridine-3′-*O*-thiophosphate methyl ester (uridine–O–P(=S)–O–CH_3)	17			
Molecule 1		66; 39	91[cd], 145[d]; 168[cf], 46[f]	91[d], 160[d]
Molecule 2		47; 33	94[cd], 145[d]; 179[cf], 69[f]	86[d], 161[d]

a. Since enantiomorphous molecules occur in all substances but the polynucleotides, only magnitudes are given (0 to 180°).
b. Within a group contained within semicolons the O–C unit is kept constant.
c. The first O is not esterified; without this superscript it is.
d. Involves O(3′) and C(3′).
e. Involves O(5′) and C(5′).
f. Involves the C(5′) analogue CH_3 group.

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Ooi & Fernando, 1967; Ito, 1972; Furlani, Tomlinson, Porta & Sgamellotti, 1970; Knox & Prout, 1969); but in the isopropyl series (Lawton & Kokotailo, 1969; Lawton, 1971), where two attached carbons must be optimally placed, compromise values in the *gauche* (120°) range occur frequently. The O–P–O–C conformation is most often *trans* or *gauche* (60°) but occasionally on the edge of the *gauche* (120°) range. As one might expect, polynucleotide P–O(5′)–C(5′)–C(4′) angles resemble those in the ethyl monomer series, while P–O(3′)–C(3′)–C(2′) and P–O(3′)–C(3′)–C(4′), due to the attached bulky ribose moiety, resemble isopropyl values.

Molecular orbital calculations

To clarify further the nature of the P–O and P–S bonds, extended Hückel (Hoffman, 1963) calculations were carried out on the diethylphosphorothioate anion. Input parameters and results are summarized in Table 5. Coordinates were taken directly from this X-ray study, orbital exponents were assigned by Burns's (1964) rules, diagonal Hamiltonian matrix elements were set to the valence state ionization potentials (VSIP) of Pilcher & Skinner (1962) for second-row elements and those of Levison & Perkins (1969) for third-row, and the Wolfsberg & Helmholz (1952) approximation was used for off-diagonal terms

$$H_{ij}=0{\cdot}5K(H_{ii}+H_{jj})S_{ij}$$

with K taken equal to 1·75 following Hoffman (1963). Calculations with and without *d* orbitals in the basis set for third-row atoms yield similar conclusions: the Mulliken charge on oxygen is considerably more negative than on sulphur, and the total overlap population of the P–S bond is about double that of the P–O bond to unesterified oxygen. The reduction of the negative charge on sulphur when *d* orbitals are included in the basis set is consistent with the concept of back donation of density *via d* orbitals. It is well known that the extended Hückel method greatly exaggerates charges, and the overlap population values depend on parametrization. Thus these results have qualitative significance only. Still a consistent picture emerges: a nearly double bond connecting P to a relatively uncharged S, and an approximately single bond between P and the unesterified O bearing a strong negative charge. This O makes an attractive ligand for the magnesium ion. One is led to speculate that in polynucleotide phosphorothioates the alkaline earth counter-ions will coordinate better on oxygen than on sulphur, and that one factor influencing behaviour of nucleoside phosphorothioate diastereomers toward enzymes is the relative position of O and S to any divalent metal ion essential for enzyme activity.

Table 5. *Input parameters and results for extended Hückel calculations on* $(EtO)_2POS^-$

	Orbital exponent			VSIP (eV)		
	s	*p*	*d*	*s*	*p*	*d*
H	1·000			13·60		
C	1·550	1·325		20·78	11·31	
O	2·200	1·975		34·35	17·86	
P	1·750	1·300	0·833	19·37	10·84	2·86
S	1·967	1·517	1·000	20·52	10·78	3·06

	Charge	Basis *s,p*	Basis *s,p,d*	Overlap Population	Basis *s,p*	Basis *s,p,d*
S		−1·0	−0·6	P–S	1·1	1·2
O		−1·6	−1·6	P–O	0·5	0·6

Conclusions

The aim of this investigation was to find a clue to the peculiar biochemical behaviour of the polynucleotide phosphorothioates for which the diethylphosphorothioate molecule served as a model. From the reported study two conclusions can be drawn.

(1) Most probably the phosphorothioate group imposes on the polynucleotide phosphorothioates a structure similar to that of C-DNA. Since it is assumed that in biochemical processes the high humidity A-DNA form is relevant, it might well be that the unusual conformation of the polynucleotide phosphorothioates is responsible for their peculiar biochemical behaviour.

(2) The negative charge on the phosphorothioate group is not evenly distributed between the sulphur and the oxygen atoms but located predominantly at the oxygen atom, in contrast to normal polynucleotides; thus the overall charge pattern is similar but the detailed pattern is different.

At present on the basis of this study these two structural effects, which may occur at the enzyme recognition or reaction level, cannot be differentiated.

Recently, the crystal structure of the triethylammonium salt of uridine-3′-*O*-thiophosphate methyl ester has been solved (Eckstein, Saenger & Suck, 1972; Saenger & Suck, in preparation). Although the cations could not be located unambiguously due to disorder, it is clear that they are positioned opposite the phosphate oxygen atom, away from the (uncharged) sulphur. The conformational angles for the thiophosphate diester group are given in Table 4; they are similar to those reported for the title compound in spite of the different substitution and thus give further evidence supporting the C-DNA structure for the polynucleotide phosphorothioates.

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The Crystal Structure of 5*H*,8*H*-Dibenzo[*d*,*f*] [1,2]-dithiocin-1,1-dioxide

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The crystal structure of 5*H*,8*H*-dibenzo[*d*,*f*] [1,2]dithiocin-1,1-dioxide, $C_{14}H_{12}S_2O_2$, has been determined by direct methods. The bridged biphenyl crystallizes in the triclinic space group $P\bar{1}$ with $a=7{\cdot}950$ (7), $b=11{\cdot}240$ (9), $c=7{\cdot}945$ (7) Å, $\alpha=91{\cdot}10$ (7), $\beta=117{\cdot}22$ (6), $\gamma=88{\cdot}86$ (7)°, $Z=2$. Intensities were collected with Mo $K\alpha$ radiation on a Syntex $P\bar{1}$ diffractometer to a maximum 2θ value of 42° by the θ–2θ scan technique. Coordinates and anisotropic temperature factors of the non-hydrogen atoms were refined by full-matrix least-squares. The final R was 0·063. The conformation of the eight-membered ring is a 'pseudo-chair'. A significant shortening of 'pseudo-axial' S–O bond lengths is observed.

Introduction

The structure of the title compound, $C_{14}H_{12}S_2O_2$, (I), is of interest as part of a program designed to determine the factors which influence conformational preferences in eight-membered ring bridged biphenyls.