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Crystal and Molecular Structure of 1,5-Dihydroxy-9-oxa-3,7-dithiabicyclo[3.3.1]nonane-3-oxide

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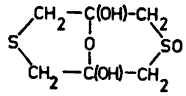
1,5-Dihydroxy-9-oxa-3,7-dithiabicyclo[3.3.1]nonane-3-oxide (DON) is orthorhombic ($Pna2_1$) with $a = 9.756$, $b = 11.996$ and $c = 7.212$ Å. The molecules have a twin-chair conformation and are linked together by hydrogen bonds between the hydroxyl groups of two different molecules and the sulphoxide oxygen. There is a very short intramolecular contact of 3.17 Å between the two sulphur atoms which leads to a deformation of two valence angles.

A product with the composition $(C_3H_5SO_2)_n$ is obtained on oxidation of 1,5-dithiacyclooctane-3,7-dione with hydrogen peroxide. Gustafsson [1] established the product to be 1,5-dihydroxy-9-oxa-3,7-dithiabicyclo[3.3.1]-nonane-3-oxide (DON, I) from chemical, IR, NMR and mass spectral data.



(I)

Eight possible combinations of ring conformations and sulphoxide configurations are possible for DON and an X-ray single crystal analysis was performed to determine the molecular structure of the oxidation product.

CRYSTAL DATA

$(C_3H_5SO_2)_2$. M = 210.26.
Orthorhombic $a = 9.756(2)$, $b = 11.996(2)$, $c = 7.212(1)$ Å.
U = 844.04 Å^3.
Z = 4.
D_c = 1.65 g cm^{-3}.
F(000) = 440.
λ = 1.54051 (Cu$K\alpha_1$ radiation).
Absent spectra $0kl$ for $(k+l)$ odd; $h0l$ for h odd;
Space group $Pna2_1$.

EXPERIMENTAL

Suitable crystals for X-ray work were grown from water. Intensities were recorded on a Picker Facs I automatic diffractometer using graphite monochromatized Cu$K\alpha$ radiation. The $\theta/2\theta$ scanning mode was used with a scan speed of 1°/min and with 10 sec background counts on each side of the peak. In total 839 peaks were measured with $2\theta < 120°$ of which 749 were considered to be above background ($< 4\sigma$). The data were corrected for the Lorentz and polarization factors but not for absorption or extinction.

STRUCTURE DETERMINATION

The sulphur positions were found from the sharpened Patterson series and the remaining non-hydrogen atoms from the sulphur phased electron density calculation. After a few cycles of full matrix least-squares refinement during which the R-value decreased to 0.07 a difference series was calculated. All hydrogens could be well located except those on the hydroxyl oxygens. Sausage-like regions of positive electron density in the difference synthesis were, however, found at the expected positions of the hydroxyl hydrogens and these were included in the following structure factor calculations with calculated positional parameters.

The full matrix refinement was then continued. An attempt to include the hydroxyl hydrogens failed as expected and they were excluded from the following refinement. Anisotropic thermal parameters were used for the non-hydrogen atoms. The refinement proceeded normally for the hydrogen positional parameters but it was not possible to refine the isotropic temperature factors. These were also excluded from the final refinement and given values corresponding to that of the parent atom. The final R-value was 0.038 for all observed reflections. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography [2] for all atoms except hydrogen for which the values of Stewart, Davidson and Simpson [3] were used. Anomalous dispersion correction was applied to the sulphur atom contribution.

The weight assigned to each observation in the least-squares refinement was

$$\omega = \frac{1}{1 + \left[\frac{|F_o| - 2.44\ F_{min}}{3.05\ F_{min}}\right]^2}$$

All calculations were performed on the dual computer system Datasaab D21-PDP 15 using programs by Abrahamsson, Aleby, Larsson, Nilsson, Selin and Westerdahl.[4]

RESULTS

The final structure factors are given in Table 1, the atomic positional and thermal parameters in Tables 2 and 3. The interatomic distances and angles are given in Fig. 1 and with standard deviations in Table 4, where also values for the hydrogens are included.

Table 1. Observed and calculated structure factors. The phase angles are given as fractions of one revolution.

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
0	2	0	580	670	0.006	6	6	0	257	262	0.005	7	10	1	59	51	0.121
0	4	0	631	639	0.504	6	7	0	304	298	0.510	6	11	1	182	187	0.402
0	6	0	90	90	0.546	6	8	0	171	169	0.511	6	10	1	161	157	0.524
0	8	0	153	153	0.508	6	9	0	56	55	0.995	6	9	1	49	47	0.563
0	10	0	241	241	0.500	6	10	0	228	244	0.510	6	8	1	174	173	0.770
0	12	0	260	259	0.505	6	11	0	108	109	0.022	6	7	1	139	134	0.027
1	13	0	71	67	0.999	7	10	0	168	165	0.009	6	6	1	157	165	0.824
1	12	0	203	204	0.509	7	9	0	25	14	0.406	6	5	1	188	170	0.296
1	11	0	70	71	0.526	7	8	0	158	154	0.515	6	4	1	180	175	0.287
1	10	0	208	204	0.503	7	7	0	49	49	0.503	6	3	1	289	265	0.412
1	9	0	279	287	0.511	7	6	0	407	397	0.510	6	2	1	180	178	0.236
1	8	0	231	243	0.009	7	5	0	264	252	0.506	6	1	1	201	203	0.438
1	7	0	334	332	0.507	7	4	0	220	200	0.510	6	0	1	241	237	0.463
1	6	0	236	226	0.008	7	3	0	16	18	0.961	5	1	1	390	381	0.981
1	5	0	333	348	0.501	7	2	0	64	65	0.004	5	2	1	67	67	0.435
1	4	0	255	254	0.990	7	1	0	150	153	0.009	5	3	1	282	278	0.354
1	3	0	484	490	0.004	8	0	0	247	262	0.006	5	4	1	348	341	0.209
1	2	0	828	957	0.504	8	1	0	221	223	0.510	5	5	1	196	186	0.562
1	1	0	63	66	0.049	8	2	0	98	77	0.500	5	6	1	232	227	0.212
2	0	0	935	980	0.500	8	3	0	326	323	0.513	5	7	1	176	172	0.674
2	1	0	418	399	1.000	8	4	0	283	292	0.506	5	8	1	197	204	0.935
2	2	0	95	88	0.019	8	5	0	79	80	0.970	5	9	1	241	235	0.866
2	3	0	117	114	0.507	8	6	0	128	128	0.507	5	9	1	238	235	0.866
2	4	0	435	434	0.008	8	7	0	70	78	0.001	5	10	1	99	102	0.818
2	5	0	72	55	0.971	8	8	0	139	147	0.010	5	11	1	127	114	0.749
2	6	0	74	58	0.490	9	8	0	25	24	0.024	5	12	1	100	107	0.573
2	7	0	102	110	0.513	9	7	0	72	75	0.013	4	12	1	100	102	0.740
2	8	0	324	328	0.513	9	6	0	109	108	0.507	4	11	1	302	294	0.856
2	9	0	169	166	0.500	9	5	0	224	238	0.008	4	10	1	266	267	0.788
2	10	0	253	253	0.518	9	4	0	273	268	0.512	4	9	1	78	77	0.376
2	11	0	231	241	0.005	9	3	0	76	74	0.003	4	8	1	238	239	0.735
2	12	0	37	26	0.975	9	2	0	305	296	0.512	4	7	1	167	172	0.430
2	13	0	40	40	0.030	10	0	0	326	348	0.509	4	6	1	68	97	0.402
3	13	0	144	138	0.504	10	1	0	84	90	0.005	4	5	1	77	66	0.837
3	12	0	236	243	0.014	10	2	0	113	112	0.514	4	4	1	128	131	0.365
3	11	0	211	209	0.505	10	3	0	51	38	0.997	4	3	1	330	336	0.153
3	10	0	48	42	0.037	10	4	0	91	97	0.011	4	2	1	283	287	0.196
3	9	0	163	156	0.510	10	5	0	174	181	0.512	4	1	1	448	449	0.062
3	8	0	232	235	0.512	10	6	0	93	99	0.017	4	0	1	833	745	0.198
3	7	0	89	87	0.523	11	2	0	36	40	0.496	3	1	1	548	558	0.382
3	6	0	528	547	0.507	11	1	0	46	44	0.507	3	2	1	113	117	0.070
3	5	0	226	214	0.993	11	1	1	113	112	0.288	3	3	1	225	235	0.043
3	4	0	104	80	0.507	11	2	1	211	225	0.829	3	4	1	428	429	0.275
3	3	0	90	85	0.488	10	6	1	125	131	0.880	3	5	1	223	245	0.910
3	2	0	116	123	0.015	10	5	1	213	226	0.758	3	6	1	615	621	0.326
3	1	0	1117	1127	0.003	10	4	1	162	164	0.934	3	7	1	227	236	0.805
4	0	0	291	237	0.476	10	3	1	144	142	0.563	3	8	1	61	63	0.550
4	1	0	338	339	0.505	10	2	1	157	158	0.301	3	9	1	214	209	0.538
4	2	0	391	399	0.006	10	1	1	48	51	0.353	3	10	1	142	132	0.604
4	3	0	263	280	0.513	10	0	1	311	323	0.286	3	11	1	88	84	0.494
4	4	0	75	77	0.532	9	1	1	186	186	0.224	3	12	1	40	33	0.747
4	5	0	244	223	0.510	9	2	1	127	122	0.502	3	13	1	111	113	0.005
4	6	0	417	416	0.507	9	3	1	130	133	0.259	2	13	1	159	168	0.621
4	7	0	47	47	0.508	9	4	1	139	134	0.480	2	12	1	49	54	0.429
4	8	0	63	56	0.504	9	5	1	207	206	0.483	2	11	1	175	180	0.607
4	9	0	98	92	0.005	9	6	1	57	53	0.966	2	10	1	34	34	0.713
4	10	0	96	100	0.007	9	7	1	141	153	0.767	2	9	1	178	181	0.926
4	11	0	25	16	0.460	9	8	1	66	68	0.895	2	8	1	75	80	0.533
4	12	0	22	19	0.543	8	9	1	50	55	0.029	2	7	1	324	338	0.021
5	12	0	51	51	0.998	8	8	1	208	211	0.757	2	6	1	305	306	0.737
5	11	0	49	48	0.527	8	7	1	138	138	0.449	2	5	1	432	450	0.185
5	10	0	146	140	0.001	8	6	1	188	180	0.629	2	4	1	336	334	0.847
5	9	0	54	47	0.548	8	5	1	38	27	0.171	2	3	1	637	645	0.292
5	8	0	96	93	0.014	8	4	1	50	49	0.415	2	2	1	271	262	0.345
5	7	0	86	83	0.511	8	3	1	302	302	0.879	2	1	1	276	270	0.391
5	6	0	121	126	0.997	8	2	1	189	189	0.197	2	0	1	151	151	0.425
5	5	0	65	66	0.016	8	1	1	146	158	0.758	1	1	1	775	833	0.166
5	4	0	479	495	0.509	8	0	1	272	275	0.110	1	2	1	528	546	0.259
5	3	0	55	53	0.025	7	1	1	444	453	0.282	1	3	1	85	81	0.949
5	2	0	356	355	0.514	7	2	1	128	127	0.114	1	4	1	259	273	0.179
5	1	0	294	266	0.499	7	3	1	76	78	0.095	1	5	1	462	489	0.385
6	0	0	247	256	0.992	7	4	1	274	277	0.766	1	6	1	270	263	0.982
6	1	0	75	77	0.501	7	5	1	260	257	0.947	1	7	1	56	54	0.652
6	2	0	43	39	0.998	7	6	1	257	259	0.775	1	8	1	165	179	0.247
6	3	0	255	255	0.505	7	7	1	109	110	0.698	1	9	1	385	388	0.817
6	4	0	251	244	0.010	7	8	1	213	222	0.388	1	10	1	65	72	0.859
6	5	0	590	579	0.505	7	9	1	199	197	0.629	1	11	1	255	271	0.862

Table 1. Continued.

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
1	12	1	211	219	0.752	6	6	2	146	138	0.328	5	9	3	186	189	0.407
1	13	1	175	175	0.427	6	7	2	85	77	0.696	5	10	3	133	134	0.773
0	13	1	179	184	0.870	6	8	2	42	30	0.833	5	11	3	129	123	0.572
0	11	1	70	72	0.905	6	9	2	95	103	0.129	4	12	3	40	39	0.816
0	9	1	212	213	0.488	6	10	2	165	173	0.734	4	11	3	50	51	0.372
0	7	1	583	596	0.369	6	11	2	114	118	0.908	4	10	3	150	152	0.753
0	5	1	528	572	0.314	7	10	2	40	29	0.805	4	9	3	47	39	0.853
0	3	1	371	408	0.895	7	9	2	101	102	0.408	4	8	3	167	171	0.559
0	1	1	36	37	0.052	7	8	2	122	123	0.754	4	7	3	173	184	0.860
0	0	2	1169	1211	0.130	7	7	2	181	179	0.417	4	6	3	156	167	0.634
0	2	2	422	457	0.009	7	6	2	226	216	0.545	4	5	3	174	168	0.949
0	4	2	469	505	0.670	7	5	2	218	212	0.821	4	4	3	155	162	0.733
0	6	2	45	44	0.934	7	4	2	371	357	0.493	4	3	3	458	461	0.244
0	8	2	425	443	0.362	7	3	2	139	141	0.861	4	2	3	256	251	0.305
0	10	2	559	585	0.476	7	2	2	376	368	0.375	4	1	3	634	606	0.270
0	12	2	78	79	0.645	7	1	2	89	89	0.416	4	0	3	364	359	0.269
1	13	2	42	33	0.349	8	0	2	314	308	0.263	3	1	3	246	229	0.840
1	12	2	71	65	0.830	8	1	2	122	122	0.628	3	2	3	162	153	0.018
1	11	2	93	92	0.341	8	2	2	47	42	0.847	3	3	3	329	322	0.269
1	10	2	238	233	0.687	8	3	2	100	90	0.682	3	4	3	478	472	0.285
1	9	2	173	171	0.495	8	4	2	135	133	0.774	3	5	3	237	240	0.309
1	8	2	256	260	0.464	8	5	2	202	201	0.286	3	6	3	71	69	0.218
1	7	2	431	441	0.476	8	6	2	89	97	0.919	3	7	3	86	89	0.741
1	6	2	154	164	0.327	8	7	2	189	196	0.367	3	8	3	20	12	0.913
1	5	2	40	37	0.011	8	8	2	26	17	0.045	3	9	3	331	338	0.759
1	4	2	212	219	0.715	8	9	2	34	30	0.463	3	0	3	80	82	0.477
1	3	2	366	386	0.961	9	7	2	46	42	0.914	3	11	3	87	84	0.584
1	2	2	655	665	0.814	9	6	2	152	152	0.443	3	12	3	74	74	0.652
1	1	2	410	438	0.895	9	5	2	107	111	0.314	2	12	3	93	92	0.673
2	0	2	793	727	0.858	9	4	2	165	162	0.433	2	11	3	265	270	0.714
2	1	2	168	154	0.451	9	3	2	175	173	0.331	2	10	3	93	89	0.416
2	2	2	363	379	0.892	9	2	2	138	139	0.768	2	9	3	67	65	0.073
2	3	2	271	262	0.122	9	1	2	52	62	0.620	2	8	3	188	194	0.757
2	4	2	321	320	0.270	10	0	2	176	194	0.661	2	7	3	415	436	0.240
2	5	2	297	292	0.248	10	1	2	154	156	0.328	2	6	3	35	141	0.779
2	6	2	323	343	0.415	10	2	2	101	106	0.505	2	5	3	332	341	0.208
2	7	2	70	70	0.449	10	3	2	184	188	0.405	2	4	3	228	223	0.140
2	8	2	167	175	0.648	10	4	2	74	76	0.371	2	3	3	276	263	0.972
2	9	2	113	106	0.038	10	5	2	187	187	0.506	2	2	3	363	345	0.998
2	10	2	82	78	0.881	10	4	3	111	107	0.311	2	1	3	117	111	0.010
2	11	2	134	130	0.141	10	3	3	146	148	0.726	2	0	3	366	345	0.166
2	12	2	72	68	0.401	10	2	3	51	51	0.309	1	1	3	526	545	0.338
2	13	2	75	76	0.966	10	1	3	35	29	0.594	1	2	3	367	381	0.262
3	13	2	36	32	0.893	10	0	3	25	27	0.300	1	3	3	96	98	0.388
3	12	2	76	74	0.309	9	1	3	243	255	0.222	1	4	3	292	303	0.035
3	11	2	207	216	0.531	9	2	3	189	184	0.769	1	5	3	451	470	0.744
3	10	2	31	28	0.313	9	3	3	87	89	0.141	1	6	3	261	280	0.144
3	9	2	304	307	0.421	9	4	3	94	102	0.649	1	7	3	237	210	0.529
3	8	2	117	124	0.816	9	5	3	146	147	0.752	1	8	3	73	76	0.216
3	7	2	112	114	0.078	9	6	3	79	80	0.391	1	9	3	26	20	0.414
3	6	2	164	170	0.758	8	8	3	157	161	0.644	1	10	3	49	42	0.577
3	5	2	122	119	0.517	8	7	3	119	121	0.685	1	11	3	86	86	0.057
3	4	2	482	474	0.399	8	6	3	228	234	0.728	1	12	3	130	131	0.708
3	3	2	71	62	0.431	8	5	3	54	55	0.591	0	13	3	107	105	0.293
3	2	2	401	419	0.378	8	4	3	129	123	0.956	0	11	3	94	95	0.281
3	1	2	425	414	0.042	8	3	3	59	54	0.347	0	9	3	132	131	0.584
4	0	2	296	279	0.605	8	2	3	271	269	0.145	0	7	3	219	235	0.786
4	1	2	36	33	0.624	8	1	3	39	36	0.641	0	5	3	295	286	0.210
4	2	2	79	57	0.214	8	0	3	393	397	0.207	0	3	3	454	497	0.257
4	3	2	269	267	0.584	7	1	3	61	55	0.258	0	1	3	331	310	0.794
4	4	2	464	479	0.915	7	2	3	249	255	0.349	0	0	4	410	377	0.885
4	5	2	282	280	0.538	7	3	3	116	126	0.303	0	2	4	346	372	0.965
4	6	2	155	155	0.727	7	4	3	128	128	0.868	0	4	4	50	55	0.221
4	7	2	194	212	0.442	7	5	3	128	119	0.332	0	6	4	414	423	0.280
4	8	2	303	293	0.427	7	6	3	189	206	0.857	0	8	4	208	211	0.396
4	9	2	117	117	0.635	7	7	3	126	138	0.590	0	10	4	345	351	0.599
4	10	2	243	237	0.327	7	8	3	87	86	0.712	0	12	4	65	63	0.352
4	11	2	100	99	0.844	7	9	3	230	250	0.720	1	12	4	151	151	0.198
4	12	2	100	95	0.391	6	10	3	204	211	0.684	1	11	4	99	103	0.278
5	12	2	295	314	0.927	6	9	3	67	58	0.387	1	10	4	30	29	0.173
5	11	2	31	27	0.253	6	8	3	163	163	0.768	1	9	4	206	205	0.370
5	10	2	196	191	0.031	6	7	3	179	169	0.271	1	8	4	312	309	0.785
5	9	2	54	54	0.854	6	6	3	69	70	0.242	1	7	4	295	305	0.519
5	8	2	200	209	0.315	6	5	3	178	166	0.279	1	6	4	148	158	0.872
5	7	2	64	71	0.735	6	4	3	180	176	0.340	1	5	4	67	60	0.264
5	6	2	380	390	0.379	6	3	3	147	153	0.762	1	4	4	47	45	0.125
5	5	2	200	196	0.342	6	2	3	117	109	0.186	1	3	4	232	232	0.941
5	4	2	78	48	0.544	6	1	3	276	272	0.790	1	2	4	334	357	0.080
5	3	2	50	49	0.976	6	0	3	264	259	0.943	1	1	4	293	305	0.832
5	2	2	120	110	0.588	5	1	3	540	524	0.176	2	0	4	286	297	0.029
5	1	2	185	192	0.891	5	2	3	184	176	0.933	2	1	4	101	101	0.598
6	0	2	301	315	0.962	5	3	3	234	219	0.932	2	2	4	95	100	0.911
6	1	2	141	142	0.423	5	4	3	140	133	0.195	2	3	4	207	198	0.273
6	2	2	96	94	0.020	5	5	3	199	197	0.791	2	4	4	204	222	0.708
6	3	2	533	535	0.420	5	6	3	245	252	0.288	2	5	4	179	194	0.407
6	4	2	273	268	0.378	5	7	3	175	172	0.732	2	6	4	222	223	0.648
6	5	2	328	318	0.518	5	8	3	112	114	0.185	2	7	4	223	222	0.416

Table 1. Continued.

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
2	8	4	177	179	0.347	6	4	5	121	129	0.572	2	9	6	83	84	0.476
2	9	4	97	90	0.261	6	3	5	154	149	0.061	3	9	6	99	97	0.224
2	10	4	264	261	0.243	6	2	5	33	24	0.784	3	8	6	127	126	0.446
2	11	4	75	76	0.640	6	1	5	112	117	0.025	3	7	6	160	165	0.313
3	11	4	171	176	0.524	6	0	5	332	343	0.105	3	6	6	159	168	0.451
3	10	4	86	86	0.724	5	1	5	54	43	0.248	3	5	6	71	70	0.416
3	9	4	135	141	0.508	5	2	5	313	320	0.095	3	4	6	160	149	0.141
3	8	4	177	166	0.230	5	3	5	239	236	0.103	3	3	6	308	316	0.661
3	7	4	282	284	0.194	5	4	5	128	123	0.139	3	2	6	201	198	0.129
3	6	4	287	281	0.269	5	5	5	151	142	0.096	3	1	6	60	62	0.904
3	5	4	86	91	0.398	5	6	5	110	107	0.199	4	0	6	204	202	0.893
3	4	4	203	205	0.543	5	7	5	103	98	0.492	4	1	6	86	84	0.627
3	3	4	32	22	0.622	5	8	5	33	32	0.048	4	2	6	196	190	0.955
3	2	4	227	244	0.596	5	9	5	297	295	0.600	4	3	6	98	104	0.413
3	1	4	249	241	0.993	4	10	5	155	155	0.640	4	4	6	98	94	0.570
4	0	4	452	436	0.738	4	9	5	115	108	0.264	4	5	6	108	118	0.362
4	1	4	92	97	0.114	4	8	5	150	158	0.592	4	6	6	128	125	0.465
4	2	4	314	292	0.784	4	7	5	272	266	0.121	4	7	6	48	45	0.016
4	3	4	115	109	0.357	4	6	5	93	97	0.542	4	8	6	118	112	0.180
4	4	4	312	321	0.141	4	5	5	206	199	0.043	5	7	6	47	46	0.096
4	5	4	101	101	0.381	4	4	5	164	162	0.050	5	6	6	168	160	0.210
4	6	4	154	145	0.236	4	3	5	147	151	0.376	5	5	6	94	100	0.006
4	7	4	80	83	0.842	4	2	5	166	163	0.049	5	4	6	233	239	0.452
4	8	4	158	157	0.556	4	1	5	234	240	0.489	5	3	6	37	36	0.159
4	9	4	77	81	0.810	4	0	5	41	37	0.234	5	2	6	228	235	0.484
4	10	4	116	118	0.500	3	1	5	331	324	0.102	5	1	6	44	37	0.937
4	11	4	115	119	0.014	3	2	5	58	59	0.740	5	0	6	151	146	0.521
5	10	4	77	78	0.862	3	3	5	170	169	0.550	6	1	6	73	73	0.403
5	9	4	92	90	0.255	3	4	5	55	54	0.244	6	2	6	134	127	0.586
5	8	4	182	174	0.531	3	5	5	219	220	0.596	6	3	6	136	135	0.261
5	7	4	20	12	0.767	3	6	5	112	114	0.232	6	4	6	73	70	0.046
5	6	4	246	258	0.544	3	7	5	123	129	0.720	6	5	6	153	151	0.318
5	5	4	149	155	0.709	3	8	5	100	100	0.683	6	6	6	78	69	0.086
5	4	4	326	308	0.302	3	9	5	109	107	0.075	7	4	6	133	136	0.285
5	3	4	109	111	0.532	3	10	5	101	103	0.683	7	3	6	97	103	0.050
5	2	4	311	317	0.337	2	10	5	58	60	0.525	7	2	6	142	139	0.138
5	1	4	92	87	0.012	2	9	5	18	15	0.327	7	1	6	101	100	0.930
6	0	4	307	302	0.184	2	8	5	64	58	0.667	5	2	7	86	90	0.038
6	1	4	211	206	0.436	2	7	5	27	16	0.296	6	1	7	69	71	0.427
6	2	4	154	155	0.165	2	6	5	109	109	0.777	6	0	7	31	30	0.205
6	3	4	297	299	0.514	2	5	5	172	172	0.106	5	1	7	213	212	0.014
6	4	4	166	168	0.676	2	4	5	72	78	0.537	5	2	7	51	49	0.267
6	5	4	196	202	0.415	2	3	5	489	501	0.120	5	3	7	111	107	0.263
6	6	4	86	81	0.601	2	2	5	222	224	0.220	5	4	7	65	62	0.214
6	7	4	192	196	0.327	2	1	5	351	348	0.119	4	5	7	129	126	0.106
6	8	4	90	91	0.210	2	0	5	155	148	0.134	4	4	7	34	29	0.412
6	9	4	23	15	0.227	1	1	5	180	176	0.660	4	3	7	101	96	0.063
7	8	4	146	144	0.170	1	2	5	181	182	0.172	4	2	7	136	141	0.953
7	7	4	138	151	0.523	1	3	5	202	206	0.095	4	1	7	85	79	0.017
7	6	4	138	135	0.293	1	4	5	274	291	0.109	4	0	7	113	115	0.957
7	5	4	146	149	0.191	1	5	5	238	244	0.123	3	1	7	109	104	0.333
7	4	4	205	197	0.466	1	6	5	183	184	0.058	3	2	7	108	107	0.949
7	3	4	192	199	0.966	1	7	5	140	147	0.673	3	3	7	74	71	0.968
7	2	4	114	104	0.601	1	8	5	135	132	0.161	3	4	7	169	180	0.035
7	1	4	158	151	0.735	1	9	5	196	199	0.641	3	5	7	130	131	0.913
8	0	4	146	140	0.718	1	10	5	45	46	0.484	3	6	7	97	93	0.256
8	1	4	53	49	0.359	1	11	5	127	127	0.574	2	6	7	62	59	0.910
8	2	4	63	63	0.455	0	11	5	205	207	0.565	2	5	7	137	134	0.032
8	3	4	204	210	0.294	0	9	5	118	127	0.764	2	4	7	64	60	0.976
8	4	4	73	65	0.315	0	7	5	133	137	0.116	2	3	7	141	149	0.331
8	5	4	169	175	0.365	0	5	5	208	212	0.234	2	2	7	129	123	0.326
8	6	4	64	56	0.173	0	3	5	310	307	0.687	2	1	7	86	81	0.358
8	7	4	140	130	0.531	0	1	5	241	238	0.733	2	0	7	168	166	0.156
9	5	4	71	72	0.677	0	0	6	413	404	0.012	1	1	7	214	215	0.943
9	4	4	123	122	0.401	0	2	6	226	237	0.735	1	2	7	91	94	0.141
9	3	4	60	55	0.385	0	4	6	280	290	0.590	1	3	7	43	34	0.617
9	2	4	197	195	0.268	0	6	6	261	272	0.435	1	4	7	81	80	0.103
9	1	4	194	190	0.283	0	8	6	160	163	0.299	1	5	7	254	257	0.469
9	1	5	27	23	0.169	1	9	6	140	143	0.396	1	6	7	144	144	0.010
8	5	5	59	61	0.358	1	8	6	228	229	0.022	1	7	7	67	62	0.746
8	4	5	157	161	0.150	1	7	6	78	77	0.429	0	7	7	113	113	0.403
8	3	5	184	181	0.670	1	6	6	106	112	0.978	0	5	7	52	52	0.210
8	2	5	177	182	0.157	1	5	6	31	27	0.360	0	3	7	380	405	0.960
8	1	5	79	80	0.832	1	4	6	47	46	0.419	0	1	7	172	185	0.953
8	0	5	74	64	0.104	1	3	6	205	209	0.055	0	0	8	74	69	0.404
7	1	5	251	257	0.125	1	2	6	208	220	0.588	0	2	8	93	99	0.789
7	2	5	204	214	0.571	1	1	6	235	239	0.827	0	4	8	174	189	0.816
7	3	5	106	100	0.995	2	0	6	245	235	0.679	1	3	8	27	18	0.319
7	4	5	23	21	0.742	2	1	6	208	208	0.166	1	2	8	168	173	0.904
7	5	5	205	206	0.631	2	2	6	75	73	0.938	1	1	8	125	130	0.824
7	6	5	64	64	0.999	2	3	6	99	100	0.290	2	0	8	214	228	0.848
7	7	5	88	91	0.560	2	4	6	212	222	0.049	2	1	8	88	93	0.381
6	8	5	49	47	0.642	2	5	6	41	38	0.390	2	2	8	85	90	0.830
6	7	5	221	222	0.628	2	6	6	133	124	0.059	2	3	8	63	62	0.288
6	6	5	89	82	0.533	2	7	6	111	109	0.403	3	1	8	61	57	0.674
6	5	5	57	56	0.466	2	8	6	128	136	0.436						

Table 2. Fractional atomic coordinates for the atoms of the structure. The standard deviations (within brackets) are multiplied by 10^5 and 10^3 for the hydrogen atoms.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B(Å^2)
S(1)	0.03554	(10)	0.05671	(8)	−0.02781	–	
S(2)	0.26446	(10)	0.10553	(8)	−0.32970	(31)	
C(1)	0.13897	(49)	0.14652	(38)	0.11652	(77)	
C(2)	0.29010	(49)	0.14270	(35)	0.06147	(77)	
C(3)	0.31653	(54)	0.18912	(37)	−0.13127	(75)	
C(4)	0.31705	(52)	−0.02840	(42)	−0.23705	(74)	
C(5)	0.28688	(50)	−0.05264	(34)	−0.03125	(89)	
C(6)	0.13455	(49)	−0.06901	(37)	0.00537	(89)	
O(1)	0.36422	(33)	0.20985	(24)	0.17951	(59)	
O(2)	0.34121	(34)	0.03268	(26)	0.08338	(59)	
O(3)	0.34999	(32)	−0.15068	(25)	0.02110	(67)	
O(4)	0.37130	(35)	0.13166	(32)	−0.47444	(54)	
H(11)	0.122	(6)	0.226	(4)	0.119	(9)	2.2
H(12)	0.130	(6)	0.115	(4)	0.252	(11)	2.2
H(31)	0.270	(6)	0.265	(5)	−0.147	(10)	2.2
H(32)	0.417	(6)	0.200	(5)	−0.173	(9)	2.2
H(41)	0.265	(6)	−0.080	(5)	−0.313	(13)	2.3
H(42)	0.425	(6)	−0.014	(5)	−0.268	(10)	2.3
H(61)	0.127	(7)	−0.105	(5)	0.142	(10)	2.5
H(62)	0.116	(7)	−0.127	(5)	−0.082	(11)	2.5
H(1)	0.361	–	0.190	–	0.330	–	2.2
H(3)	0.450	–	−0.148	–	0.064	–	2.5

Apart from the hydroxyl hydrogen atoms and the sulphur oxygen there is nearly an *mm* symmetry in the molecule (*cf.* Table 4). As earlier found for the carbocyclic bicyclo[3.3.1]nonane skeleton (Brown, Martin and Sim,[5] Webb and Becker [6]), the molecule exists in the twin-chair conformation. The following

Table 3. Anistropic thermal parameters in the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13})]$. The standard deviations (within brackets) have been multiplied by 10^4.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
S(1)	0.0169(6)	0.0250(6)	0.0388(7)	0.0000(5)	−0.0025(5)	0.0006(4)
S(2)	0.0214(6)	0.0258(6)	0.0202(6)	0.0012(5)	0.0002(5)	−0.0010(4)
C(1)	0.0249(24)	0.0206(22)	0.0334(28)	−0.0040(19)	0.0086(19)	−0.0029(18)
C(2)	0.0184(20)	0.0150(22)	0.0277(25)	0.0010(19)	0.0004(20)	0.0026(19)
C(3)	0.0302(28)	0.0213(23)	0.0253(25)	0.0006(20)	−0.0009(22)	0.0001(20)
C(4)	0.0281(26)	0.0264(22)	0.0251(26)	−0.0004(20)	0.0014(23)	0.0078(21)
C(5)	0.0275(25)	0.0136(20)	0.0342(29)	0.0057(19)	0.0053(25)	−0.0012(18)
C(6)	0.0192(21)	0.0181(19)	0.0402(31)	−0.0010(23)	0.0061(23)	0.0055(18)
O(1)	0.0308(18)	0.0265(15)	0.0225(17)	−0.0020(16)	−0.0019(17)	−0.0095(12)
O(2)	0.0232(16)	0.0186(15)	0.0244(16)	0.0023(14)	−0.0040(14)	0.0044(12)
O(3)	0.0247(16)	0.0155(15)	0.0499(25)	0.0082(15)	−0.0005(17)	0.0045(13)
O(4)	0.0217(17)	0.0479(20)	0.0212(19)	0.0042(17)	0.0039(15)	−0.0022(17)

Table 4. Interatomic distances and angles, with e.s.d.'s.

S(1) – C(1)	1.806 Å	(0.005)	C(2) – C(3)	1.519	(0.008)
– C(6)	1.807	(0.005)	– O(1)	1.377	(0.006)
S(2) – C(3)	1.820	(0.005)	– O(2)	1.420	(0.005)
– C(4)	1.814	(0.005)	C(4) – C(5)	1.541	(0.008)
– O(4)	1.508	(0.004)	C(5) – C(6)	1.522	(0.007)
C(1) – C(2)	1.528	(0.007)	– O(2)	1.418	(0.006)
			– O(3)	1.380	(0.005)

C(1) – S(1) – C(6)	97.1°	(0.2)	C(2) – C(3) – S(2)	118.0	(0.3)
C(3) – S(2) – C(4)	96.9	(0.2)	S(2) – C(4) – C(5)	117.9	(0.3)
C(3) – S(2) – O(4)	103.7	(0.2)	C(2) – O(2) – C(5)	118.3	(0.4)
C(4) – S(2) – O(4)	104.1	(0.2)	C(4) – C(5) – C(6)	112.2	(0.5)
S(1) – C(1) – C(2)	111.8	(0.4)	O(2) – C(5) – C(6)	110.9	(0.4)
C(1) – C(2) – C(3)	113.0	(0.4)	O(3) – C(5) – C(6)	106.2	(0.4)
C(1) – C(2) – O(1)	109.2	(0.4)	O(2) – C(5) – O(3)	106.8	(0.4)
C(3) – C(2) – O(1)	105.2	(0.4)	C(4) – C(5) – O(3)	109.8	(0.4)
O(1) – C(2) – O(2)	106.9	(0.4)	C(4) – C(5) – O(2)	110.7	(0.4)
C(3) – C(2) – O(2)	112.5	(0.4)			
C(1) – C(2) – O(2)	109.8	(0.4)	C(5) – C(6) – S(1)	113.0	(0.3)

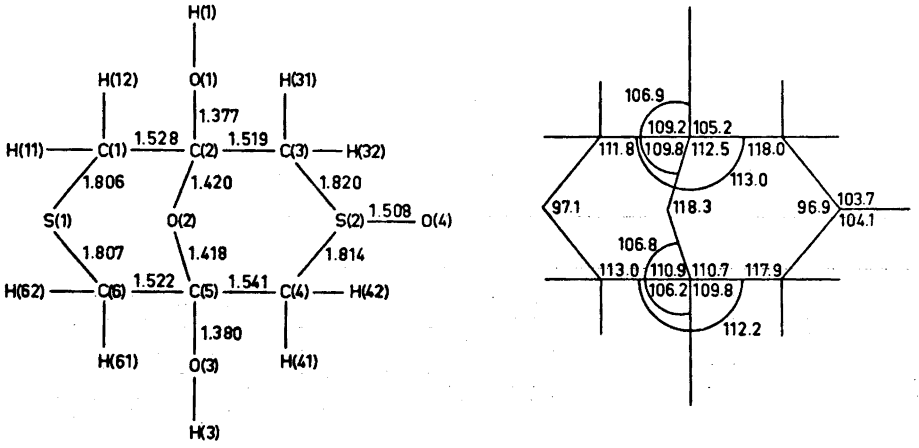


Fig. 1. Interatomic distances and angles of DON. The atomic numbering is also indicated.

Fig. 2. Stereoscopic pair of DON.

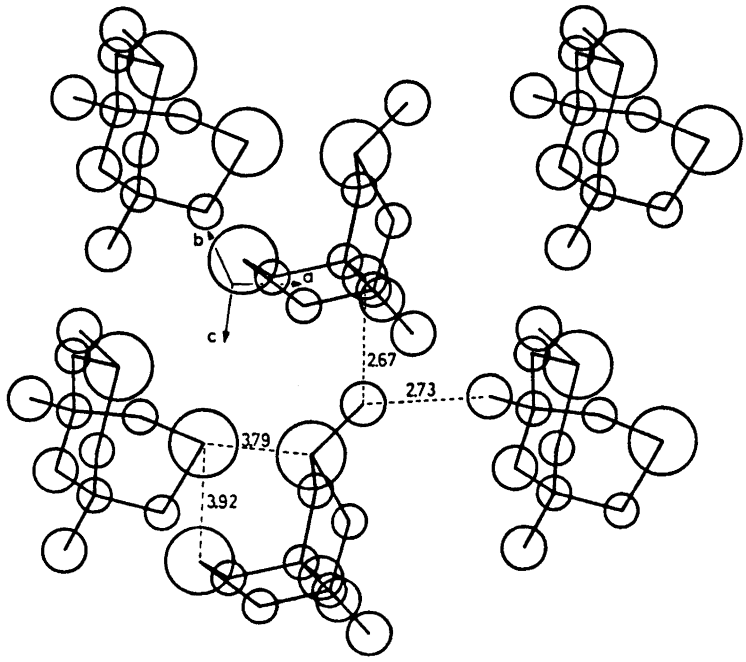


Fig. 3. Illustration of the molecular packing of DON (*cf.* also Table 7).

Table 5. Various least-squares planes in the molecule.

Planes				Equations
(a)	C(1)	C(2)	C(5) C(6)	$0.27717X - 0.43196Y + 0.85825Z - 0.07347 = 0$
(b)	C(2)	C(3)	C(4) C(5)	$0.98938X - 0.06781Y + 0.12856Z - 0.28431 = 0$
(c)	C(2)	O(2)	C(5)	$-0.78723X - 0.25379Y + 0.56201Z + 0.23004 = 0$
(d)	S(1)	O(2)	S(2)	$0.01528X + 0.98517Y + 0.17090Z - 0.05166 = 0$
(e)	S(1)	C(1)	C(6)	$-0.65394X - 0.33613Y + 0.67778Z + 0.06115 = 0$
(f)	S(2)	C(3)	C(4)	$0.93804X + 0.15336Y - 0.31072Z - 0.36671 = 0$

Deviations from the planes (Å)

	(a)	(b)	(c)	(d)	(e)	(f)
C(1)	0.014	−1.375	1.305	1.342		
C(2)	−0.015	0.009		1.214	−1.135	−0.865
C(3)	−1.412	−0.008	−1.234	1.369		
C(4)	−1.386	0.008	−1.275	−1.349		
C(5)	0.015	−0.009		−1.222	−1.094	−0.904
C(6)	−0.014	−1.414	1.267	−1.365		
O(1)			−0.079	2.238		
O(2)	0.616	0.599			−0.980	−0.636
O(3)			0.040	−2.236		
O(4)		0.127		0.030		
S(1)	−0.878		1.507			
S(2)		−0.700	−1.666			

Table 6. Magnitudes and directions (in degrees), relative to the crystal axes, of the principal vibration ellipsoids.

	axis i	B_i(Å)²	*a*	*b*	*c*		axis i	B_i(Å)²	*a*	*b*	*c*
S(1)	1	1.31	8	97	90	C(5)	1	2.02	153	65	80
	2	3.08	90	90	176		2	3.00	75	79	19
	3	1.98	89	6	90		3	0.92	78	28	106
S(2)	1	1.68	161	101	105	C(6)	1	1.85	131	75	135
	2	2.07	98	16	104		2	3.30	137	90	46
	3	1.57	108	79	21		3	0.97	79	15	80
C(1)	1	1.56	51	59	54	O(1)	1	1.37	56	39	73
	2	3.16	123	104	37		2	3.03	47	129	68
	3	1.51	124	35	97		3	1.90	62	99	152
C(2)	1	1.56	152	90	118	O(2)	1	1.88	116	44	57
	2	2.19	118	90	28		2	2.21	130	80	138
	3	1.07	89	6	90		3	1.12	129	133	68
C(3)	1	2.40	10	100	90	O(3)	1	2.08	160	90	110
	2	1.99	90	98	8		2	4.09	109	77	23
	3	1.68	100	167	98		3	0.95	89	13	102
C(4)	1	2.00	90	42	127	O(4)	1	1.99	138	90	49
	2	2.77	78	49	44		2	3.84	90	9	82
	3	1.51	167	90	78		3	1.33	132	82	137

average distances are found: C–C 1.528 Å (σ=0.007), C–H 1.02 Å (σ=0.07), C–S 1.806 Å (σ=0.005), C–S (sulphoxide) 1.817 Å (σ=0.005), C–O 1.419 Å (σ=0.006) and C–O (hydroxyl) 1.378 Å (σ=0.006). The difference in the two types of C–S bonds may not be significant ($\sim 3\ \sigma$) but is plausible with the change in the sulphur coordination number.

There is a considerable strain in the molecule at C(3) and C(4) which is evident from the difference of over 5° in the bond angles as compared with those at C(1) and C(6). This is no doubt caused by the very short intramolecular S···S contact of 3.17 Å. This is another case where the sulphur van der Waals

Table 7. Intermolecular H···H and S···H contacts less than 3 Å. i, ii, and iii refer to the equivalent positions $x, y, z; -x, -y, \frac{1}{2}+z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$.

A	B	Unit translation on atom B	Å
H(11)	H(41^{iii})	(0, 0, 0)	2.63
H(12)	H(62^{ii})	(0, 0, 0)	2.69
H(31)	H(61^{iii})	(0, 0, −1)	2.39
H(32)	H(61^{iii})	(0, 0, −1)	2.73
H(32)	H(3^{ii})	(1, 0, −1)	2.38
H(42)	H(3^{ii})	(1, 0, −1)	2.60
H(62)	H(1^{iii})	(0, −1, −1)	2.30
H(1)	H(3^{ii})	(1, 0, 0)	2.55
S(1)	H(61^{ii})	(0, 0, −1)	2.92
S(2)	H(1^{i})	(0, 0, −1)	2.82
S(2)	H(3^{ii})	(1, 0, −1)	2.93

radius is found to be considerably shorter than 1.85 (*cf.* Lynch, Mellor and Nyburg [7]). In the carbocyclic bicyclo[3.3.1]nonane skeleton there is similarly a strong non-bonded interaction (about 3.1 Å) between the carbon atoms that correspond to S(1) and S(2). It is not clear from the other steric interactions why, in this particular case, the major flattening of the molecule has taken place at C(3) and C(4). S(2) is thus displaced 0.878 Å out of the plane through C(2), C(3), C(4) and C(5) whereas S(1) is only 0.700 Å out of the C(1), C(2), C(5), C(6) plane. The planes through S(1), C(2), C(6) and S(2), C(3), C(4) are intersected by the plane through C(2), C(5), O(2) at angles of 11° and 20°, respectively. The planes would of course have been parallel in an idealized twin-chair conformation.

The two hydroxyl oxygen atoms are close to the plane through C(2), O(2), C(5). O(3) is 0.040 Å on one side and O(1) 0.079 Å on the other. The sulphoxide oxygen is also very close (0.030 Å) to the plane through S(1), O(2) and S(2).

The molecular packing is illustrated in Fig. 3. The molecules are linked by hydrogen bonds between the hydroxyl groups and the sulphoxide oxygen. The O(1)···O(4) distance is 2.67 Å and the O(3)···O(4) distance is 2.73 Å. The C(2)−O(1)···O(4) angle is 112.7° and the C(5)−O(3)···O(4) angle is 112.1°. The S(2)−O(4)···O(3) and S(2)−O(4)···O(1) angles are 135.6° and 134.7°, respectively.

The closest intermolecular S−S contacts are 3.79 Å (S(1)···S(2)) and 3.92 Å (S(1)−S(1)). Other short packing contacts of about 2.9 Å to the sulphur atoms involve H(61) and the two hydroxyl hydrogens. The most important van der Waals H···H interactions are listed in Table 5.

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