59. *The Crystal and Molecular Structure of Dithio-oxamide (Rubeanic Acid).*

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The structure of rubeanic acid (dithio-oxamide) has been determined by three-dimensional *X*-ray diffraction methods. The crystals are triclinic with $a = 5{\cdot}858$, $b = 10{\cdot}757$, $c = 3{\cdot}936$ Å, $\alpha = 92°\ 30'$, $\beta = 102°\ 45'$, $\gamma = 92°\ 19'$. The space group is $P\bar{1}$ with two molecules in the unit cell, each lying on a centre of symmetry. The molecular parameters obtained from a least-squares refinement of 832 independent reflexions ($R = 7{\cdot}1\%$) show significant differences between the C–S and C–N distances in the two non-equivalent molecules. The central C–C bonds both have lengths equal to the standard distance between sp^2-hybridized carbon atoms.

A preliminary account of the structure of dithio-oxamide, $H_2N{\cdot}CS{\cdot}CS{\cdot}NH_2$, has appeared.[1] The present paper describes a more accurate determination of the cell dimensions, atomic co-ordinates, and thermal parameters. Since its first preparation by Gay-Lussac,[2] dithio-oxamide has played a considerable part in the early development of theories of tautomerism,[3] and has been useful as a chelating agent.[4] The molecule is of considerable theoretical interest since, as far as the number of valency electrons is concerned, it is isoelectronic with diboron tetrachloride, oxamide, the oxalate ion, and dinitrogen tetroxide.

Experimental

$C_2H_4N_2S_2$, $M = 120{\cdot}2$, Triclinic, $a = 5{\cdot}858 \pm 0{\cdot}003$, $b = 10{\cdot}757 \pm 0{\cdot}005$, $c = 3{\cdot}936 \pm 0{\cdot}003$ Å, $\alpha = 92°\ 30' \pm 0{\cdot}5'$, $\beta = 102°\ 45' \pm 1{\cdot}0'$, $\gamma = 92°\ 19' \pm 0{\cdot}5'$, $U = 241{\cdot}7$ Å,[3] $D_m = 1{\cdot}66$, $Z = 2$, $D_c = 1{\cdot}651$, $F(000) = 124$. Space group $P\bar{1}$ (C_i^1, No. 2). Single-crystal Weissenberg and Straumanis photographs. The specimen was a commercial sample recrystallized from pyridine.

The cell dimensions were determined from Straumanis photographs. Fourteen different reflexions were measured, and an iterative procedure applied in order to produce the most consistent results. Independent observations of the same reciprocal cell dimensions agreed extremely well, and it is thought that the errors quoted above for the real cell dimensions, which were obtained with λ for Cu-$K_{\alpha 1} = 1{\cdot}54050$ Å, are the maximum possible.

Equi-inclination Weissenberg photographs were taken with Cu-K_α radiation round the three principal axes with the multiple-film technique. Small crystals with a maximum dimension of 0·1 mm. were obtained by cutting and dissolution in order to minimize errors due to absorption ($\mu = 88{\cdot}1$ cm.$^{-1}$). The different layer lines were placed on the same relative scale by the method previously described.[5] 832 independent reflexions out of a possible 1070 were observed to be non-zero.

The structure was solved in projection down the [*a*] and [*c*] axes by Patterson and Fourier transform methods. Considerable time was spent in reaching the conclusion that the asymmetric unit consisted of two half-molecules rather than one whole molecule. After the solution of the phase problem, each projection was refined by Fourier and difference syntheses to *R*-factors of 11·5% and 14·1% for the *hk*0 and 0*kl* projections, respectively. The resulting co-ordinates were then refined by differential syntheses on the Manchester University (Mark II) computer with the programmes of Ahmed and Cruickshank.[6] Isotropic temperature factors were used, and the *R*-factor at this stage was 10·8%. Recently the structure was completely refined with anisotropic temperature factors on an Elliott 803 computer with the programmes of Daly,

[1] Long, Markey, and Wheatley, *Acta Cryst.*, 1954, **7**, 140.
[2] Gay-Lussac, *Ann. Chim.*, 1815, **95**, 136.
[3] Wollner, *J. prakt. Chem.*, 1884, **29**, 129.
[4] Ray, *Z. analyt. Chem.*, 1929, **79**, 94; Ewens and Gibson, *J.*, 1949, 431; Malyuga, *Zhur. analyt. Khim.*, 1955, **10**, 107.
[5] Wheatley, *Acta Cryst.*, 1954, **7**, 68.
[6] Ahmed and Cruickshank, *Acta Cryst.*, 1953, **6**, 765.

Stephens, and Wheatley.[7] The least-squares programme uses the block diagonal approximation, and standard deviations were obtained from the 3×3 and 6×6 inverse error matrices. The final R-factor for the 832 observed reflexions was 7·1%. The scattering factors were taken from International Tables.

Results

The final atomic co-ordinates are given in Table 1, together with the orthogonal co-ordinates referred to a set of axes in which $[b']$ coincides with the original triclinic axis $[b]$; $[a']$ is the projection of the original $[a]$ on to the plane perpendicular to $[b]$, and $[c']$ is perpendicular to $[a']$ and $[b']$. The thermal parameters are given in Table 2. Table 3 gives structure factors obtained from the parameters in Tables 1 and 2. The two planes marked by an asterisk were omitted from the refinement cycles because of the low calculated values.

Table 1.

Atomic co-ordinates and orthogonal co-ordinates in Å. Each co-ordinate is followed by its standard deviation quoted as units in the last place; thus, 1·0224 (45) means 1·0224 ± 0·0045.

	X	Y	Z	X'	Y'	Z'
S(1)	−1·7500 (12)	−1·4007 (12)	−0·4260 (14)	−1·6537	−1·3114	−0·4149
S(2)	−1·3350 (12)	3·9164 (12)	0·6618 (14)	−1·4813	3·9415	0·6445
N(1)	−1·0832 (47)	1·0224 (45)	−1·1797 (51)	−0·8197	1·1176	−1·1489
N(2)	−1·4624 (46)	6·3652 (46)	1·6253 (55)	−1·8231	6·3534	1·5829
C(1)	−0·7316 (44)	−0·0465 (48)	−0·4492 (49)	−0·6310	0·0027	−0·4375
C(2)	−0·7471 (46)	5·3052 (49)	1·5547 (49)	−1·0926	5·2676	1·5142

Table 2.

Thermal parameters in Å². Each parameter is followed by its standard deviation quoted as units in the last place; thus, 0·0076 (11) means 0·0076 ± 0·0011.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
S(1)	0·0245 (5)	0·0318 (6)	0·0374 (7)	−0·0059 (9)	0·0076 (11)	0·0017 (10)
S(2)	0·0289 (6)	0·0313 (6)	0·0359 (7)	0·0000 (9)	−0·0123 (11)	−0·0020 (11)
N(1)	0·0327 (22)	0·0331 (22)	0·0448 (28)	0·0072 (34)	0·0234 (41)	−0·0004 (40)
N(2)	0·0302 (21)	0·0361 (23)	0·0517 (29)	0·0129 (35)	−0·0105 (43)	0·0023 (41)
C(1)	0·0231 (23)	0·0314 (22)	0·0239 (23)	0·0050 (33)	−0·0072 (36)	0·0072 (38)
C(2)	0·0268 (24)	0·0306 (22)	0·0233 (23)	0·0038 (34)	0·0061 (37)	0·0083 (39)

The bond lengths and angles obtained from the co-ordinates in Table 1 are shown in Table 4 with their standard deviations, for the two independent molecules. The most striking fact is that the lengths of the C–S and C–N bonds appear to be different in the two molecules. In molecule 2 both bonds are shorter than the corresponding bonds in molecule 1, the C–S bond significantly so. There seems to be no obvious physical reason for this. It is unlikely, in view of the low temperature factors (the overall isotropic temperature factor B is only 2·35 Å²), that rotational and vibrational corrections[8] could account for the differences. The similarity in thermal factors and in orientations of the two molecules implies that any such corrections would have to be applied equally to both molecules. It is, perhaps, possible that the close approach of two carbon atoms to the nitrogen atom of molecule 1 in some way extracts electron-density from the π-bonded system, thus weakening and lengthening the C–S and C–N bonds. However, this hypothesis is not advanced with any great seriousness, and one is left with one of two discouraging conclusions: either there are systematic errors in the observed intensities that are not reflected in the standard deviations of the atomic positions, or these differences in bond lengths are real but for a reason that is not clear. In view of this uncertainty, it was thought justifiable to obtain the means of the values of the parameters obtained for the two molecules to give the results shown in Fig. 1.

[7] Daly, Stephens, and Wheatley, 1963, Monsanto Research S.A. (MRSA) Final Report No. 52.
[8] Cruickshank, *Acta Cryst.*, 1956, **9**, 754, 757.

TABLE 3.

Observed and calculated structure factors on a scale 100× absolute.

h	*k*	*l*	F_o	F_c	F_o-F_c	*h*	*k*	*l*	F_o	F_c	F_o-F_c	*h*	*k*	*l*	F_o	F_c	F_o-F_c
0	2	0	2228	2423	-195	5	3	0	1262	1185	77	1	-8	-1	-349	-221	-128
0	3	0	143	98	45	5	4	0	365	302	67	1	-9	-1	1191	1106	85
0	4	0	-3593	-4021	428	5	5	0	-133	-47	-86	1	-10	-1	1324	1293	31
0	5	0	-345	-298	-51	5	6	0	174	231	-57	2	0	1	-811	-685	-126
0	6	0	790	738	52	5	7	0	-1057	-1099	42	2	1	1	667	514	153
0	8	0	2536	2631	-95	5	8	0	-770	-756	-14	2	3	1	718	574	144
0	9	0	420	357	63	5	9	0	256	205	51	2	4	1	862	731	131
0	12	0	-472	-489	17	5	-1	0	-1324	-1233	-91	2	5	1	-2341	-2250	-91
0	13	0	-256	-252	-4	5	-2	0	482	324	158	2	6	1	-431	-267	-164
1	0	0	1386	1493	-107	5	-3	0	1273	1165	108	2	7	1	-729	-732	3
1	1	0	-338	-317	-21	5	-4	0	-554	-459	-95	2	8	1	-708	-657	-51
1	2	0	-1560	-1733	173	5	-5	0	1180	1104	76	2	9	1	1283	1208	75
1	3	0	554	524	30	5	-6	0	-1016	-968	-48	2	10	1	369	306	63
1	4	0	2495	2698	-203	5	-7	0	-1191	-1156	-35	2	11	1	-195	-210	15
1	6	0	2566	2604	-38	5	-8	0	-184	-164	-20	2	12	1	564	431	133
1	7	0	-390	-296	-94	5	-9	0	-770	-805	35	2	0	-1	-1683	-1994	311
1	8	0	-1488	-1396	-92	5	-10	0	143	177	-34	2	1	-1	-420	-360	-60
1	10	0	-1416	-1301	-115	6	0	0	-359	-313	-46	2	2	-1	1961	1960	1
1	11	0	195	167	28	6	1	0	1653	1746	-93	2	3	-1	903	776	127
1	12	0	1160	1084	76	6	2	0	513	419	94	2	4	-1	1704	1678	26
1	-1	0	-523	-540	17	6	3	0	277	230	47	2	5	-1	1817	1749	68
1	-2	0	4014	4606	-592	6	4	0	462	399	63	2	6	-1	-1920	-1864	-56
1	-3	0	883	939	-56	6	5	0	-1458	-1471	13	2	8	-1	-1273	-1184	-89
1	-4	0	-821	-806	-15	6	6	0	-379	-291	-88	2	9	-1	-954	-902	-52
1	-5	0	431	413	18	6	7	0	-195	-152	-43	2	10	-1	1201	1223	-22
1	-6	0	-1642	-1831	189	6	-1	0	-316	-296	-22	2	11	-1	369	314	55
1	-7	0	-534	-647	87	6	-2	0	-338	-311	-27	2	12	-1	739	724	15
1	-8	0	1827	1840	-13	6	-3	0	-1345	-1438	93	2	13	-1	503	626	-123
1	-9	0	-328	-293	-35	6	-4	0	112	119	-7	2	-1	1	-3337	-3535	198
1	-10	0	2033	2013	20	6	-5	0	308	319	-11	2	-2	1	482	392	90
1	-11	0	667	560	107	6	-7	0	745	747	-2	2	-3	1	-1365	-1353	-12
1	-12	0	-451	-429	-22	7	0	0	297	246	51	2	-4	1	605	537	68
2	0	0	-4805	-5576	771	7	1	0	308	262	26	2	-5	1	2402	2630	-228
2	1	0	2012	2156	-144	7	2	0	236	183	53	2	-6	1	-379	-324	-55
2	2	0	1016	926	90	7	3	0	-790	-840	50	2	-7	1	523	448	75
2	3	0	1221	1225	-4	7	-1	0	944	908	36	2	-8	1	-420	-396	-24
2	4	0	3316	3781	-465	7	-2	0	297	249	48	2	-9	1	-2022	-2134	112
2	5	0	-1026	-994	-32	7	-3	0	-646	-599	-47	*2	-10	1	287	19	268
2	6	0	-831	-787	-44	7	-4	0	246	209	37	2	-11	1	-544	-504	-40
2	7	0	-462	-492	10	0	0	1	1745	1958	-213	2	-13	1	729	899	-170
2	8	0	-1856	-1987	129	0	1	1	523	377	146	2	-1	-1	1150	1186	-36
2	9	0	441	396	45	0	2	1	359	236	123	2	-2	-1	-349	-270	-79
2	10	0	646	495	151	0	3	1	-143	-90	-53	2	-3	-1	1252	1141	111
2	11	0	154	150	4	0	4	1	-1899	-1819	-80	2	-4	-1	2063	2281	-218
2	12	0	595	588	7	0	5	1	2361	2182	179	2	-6	-1	-575	-514	-61
2	-1	0	-1283	-1336	53	0	6	1	708	606	102	2	-7	-1	431	391	40
2	-2	0	-1262	-1320	58	0	7	1	739	661	58	2	-8	-1	-1899	-1906	7
2	-3	0	-1827	-1865	38	0	8	1	1642	1510	132	2	-9	-1	1047	972	75
2	-4	0	3265	3521	-256	0	9	1	-1191	-1074	-117	2	-10	-1	533	475	58
2	-5	0	965	909	56	0	10	1	-626	-526	-100	2	-11	-1	369	322	47
2	-6	0	821	706	115	0	12	1	-893	-907	14	2	-12	-1	1170	1172	-2
2	-7	0	975	831	144	0	13	1	893	844	49	2	-13	-1	-133	-96	-37
2	-8	0	-1355	-1256	-99	0	-1	1	3675	4312	-637	3	1	1	1037	1014	23
2	-9	0	-821	-740	-81	0	-2	1	-1868	-1712	-156	3	2	1	225	215	10
2	-10	0	349	275	74	0	-3	1	1150	1260	-110	3	3	1	-3183	-3597	414
2	-11	0	-318	-319	1	0	-4	1	-1581	-1721	140	*3	4	1	-277	-67	-210
2	-12	0	595	615	-20	0	-5	1	-1971	-2081	110	3	5	1	-1930	-2016	86
2	-13	0	420	463	-43	0	-6	1	1283	1295	-12	3	6	1	-349	-293	-56
3	0	0	-718	-629	-89	0	-7	1	564	505	59	3	7	1	1478	1477	1
3	1	0	862	726	136	0	-8	1	1098	1128	-30	3	9	1	390	374	16
3	2	0	965	814	151	0	-9	1	2382	2347	35	3	10	1	174	216	-42
3	3	0	-1232	-1122	-110	0	-10	1	-687	-679	-8	3	11	1	-1119	-1216	97
3	4	0	-1745	-1734	-11	0	-11	1	359	349	10	3	0	-1	1694	1647	47
3	6	0	-1714	-1687	-27	0	-12	1	-616	-630	14	3	1	-1	-523	-474	-49
3	7	0	1180	1057	123	0	-13	1	-749	-755	6	3	2	-1	3429	3554	-125
3	8	0	1016	892	124	1	0	1	-338	-256	-82	3	3	-1	708	667	41
3	10	0	616	535	81	1	1	1	-3347	-3456	109	3	4	-1	-1067	-1001	-66
3	11	0	-687	-656	-31	1	2	1	-2803	-2743	-60	3	6	-1	-1796	-1834	38
3	12	0	-1047	-1070	23	1	3	1	3121	3300	-179	3	7	-1	-790	-791	1
3	-1	0	1068	1036	32	1	5	1	2289	2273	16	3	8	-1	883	827	56
3	-2	0	-2433	-2493	60	1	6	1	1745	1724	21	3	10	-1	708	739	-31
3	-3	0	-1560	-1516	-44	1	7	1	-1714	-1757	43	3	11	-1	266	252	14
3	-4	0	297	234	63	1	9	1	-1037	-1045	8	3	12	-1	-503	-526	23
3	-5	0	-975	-927	-48	1	10	1	-965	-894	-71	3	-1	1	2002	2145	-143
3	-6	0	1406	1411	-5	1	11	1	698	701	-3	3	-3	1	-1879	-2079	200
3	-7	0	1355	1394	-39	1	12	1	225	248	-23	3	-5	1	-1981	-2105	124
3	-8	0	-862	-811	-51	1	0	-1	-872	-799	-73	3	-6	1	-256	-204	-52
3	-9	0	687	640	47	1	1	-1	3542	4088	-546	3	-7	1	657	607	50
3	-10	0	-1314	-1301	-13	1	2	-1	-4363	-4442	79	3	-11	1	-965	-1028	63
3	-11	0	-811	-922	111	1	3	-1	-1304	-1235	-69	3	-1	-1	-872	-932	60
3	-12	0	102	169	-67	1	4	-1	318	275	43	3	-2	-1	-3532	-3573	41
4	0	0	1191	1220	-29	1	5	-1	-338	-245	-93	3	-3	-1	256	213	43
4	1	0	-2265	-2363	94	1	6	-1	1817	1823	-12	3	-4	-1	-1345	-1338	-7
4	2	0	-1642	-1570	-72	1	7	-1	1889	1963	-74	3	-5	-1	544	482	62
4	3	0	-883	-849	-34	1	8	-1	-441	-379	-62	3	-6	-1	2146	2187	-41
4	4	0	-2094	-2218	124	1	9	-1	595	569	26	3	-8	-1	533	491	42
4	5	0	1622	1671	-49	1	10	-1	-616	-588	-28	3	-10	-1	-1108	-1084	-24
4	6	0	410	324	86	1	11	-1	-544	-522	-22	4	0	1	-523	-404	-119
4	7	0	533	463	70	1	12	-1	441	418	23	4	1	1	-1683	-1674	-9
4	8	0	646	633	13	1	13	-1	400	353	47	4	3	1	-1221	-1229	8
4	9	0	-852	-876	24	1	-1	1	-3470	-3780	310	4	5	1	1108	1123	-15
4	10	0	-821	-817	-4	1	-2	1	2351	2148	203	4	9	1	-1252	-1348	96
4	11	0	-112	-120	8	1	-3	1	2669	2763	-94	4	0	-1	1581	1457	124
4	-1	0	662	825	37	1	-4	1	318	215	103	4	1	-1	-708	-562	-126
4	-2	0	328	230	98	1	-5	1	2197	2082	115	4	2	-1	-1375	-1313	-62
4	-3	0	1920	1971	-51	1	-6	1	-965	-821	-164	4	3	-1	-595	-635	40
4	-4	0	-1796	-1818	22	1	-7	1	-1304	-1270	-34	4	4	-1	-1098	-1025	-73
4	-5	0	-821	-732	-89	1	-9	1	-266	-207	-59	4	5	-1	-533	-540	7
4	-6	0	-975	-881	-94	1	-10	1	225	144	81	4	6	-1	1601	1647	-46
4	-7	0	-1160	-1041	-119	1	-11	1	1170	1103	67	4	8	-1	811	771	40
4	-8	0	133	143	-10	1	-1	-1	4538	5017	-479	4	9	-1	-205	-163	-42
4	-9	0	626	640	-14	1	-2	-1	4723	4974	-251	4	10	-1	-1016	-1167	151
4	-10	0	-297	-320	23	1	-3	-1	-616	-483	-133	4	11	-1	-349	-396	47
4	-11	0	277	343	-66	1	-4	-1	1006	897	109	4	-1	1	1416	1337	79
4	-12	0	-246	-376	130	1	-5	-1	-1098	-975	-123	4	-3	1	821	666	155
5	0	0	-595	-514	-81	1	-6	-1	-2484	-2642	158	4	-4	1	646	525	121
5	1	0	-739	-633	-106	1	-7	-1	1437	1391	46	4	-5	1	-2156	-2310	154
5	2	0	-944	-855	-89												

TABLE 3. (*Continued.*)

h	k	l	F_o	F_c	F_o-F_c	h	k	l	F_o	F_c	F_o-F_c	h	k	l	F_o	F_c	F_o-F_c
4	−7	1	−1180	−1250	70	1	6	−2	831	663	146	3	−11	2	−487	−450	153
4	−6	1	−451	−427	−24	1	3	−2	−3016	−3117	99	3	−1	−2	−1456	−1450	−6
4	−5	1	924	984	−60	1	4	−2	750	608	142	3	−2	−2	−349	−374	25
4	−11	1	277	293	−16	1	5	−2	482	344	138	3	−3	−2	482	452	30
4	−1	−1	−441	−424	−17	1	6	−2	698	638	60	3	−5	−2	995	966	29
4	−2	−1	472	406	66	1	7	−2	2278	2334	−55	3	−6	−2	1221	1264	−43
4	−3	−1	−308	−206	−102	1	8	−2	716	633	85	3	−7	−2	−790	−853	63
4	−4	−1	−1827	−1809	−18	1	10	−2	266	244	22	3	−8	−2	503	477	26
4	−5	−1	−492	−420	−72	1	11	−2	−1198	−1345	237	3	−9	−2	−605	−551	−54
4	−7	−1	−544	−565	21	1	−1	2	−369	−327	−42	3	−10	−2	−472	−482	10
4	−8	−1	1540	1550	−50	1	−2	2	−1324	−1330	6	3	−11	−2	739	750	−11
5	0	1	328	277	51	1	−3	2	2657	2774	−115	3	−12	−2	123	120	3
5	1	1	−706	−646	−62	1	−4	2	636	584	52	4	0	2	−1601	−1675	74
5	2	1	718	697	21	1	−5	2	195	208	−13	4	1	2	−893	−835	−58
5	3	1	1745	1675	−130	1	−6	2	759	612	147	4	2	2	544	390	154
5	4	1	−277	−292	15	1	−7	2	−2135	−2121	−14	4	3	2	−626	−575	−51
5	5	1	708	581	127	1	−8	2	−924	−876	−48	4	4	2	1550	1568	−18
5	6	1	−585	−511	−74	1	−9	2	−277	−283	6	4	5	2	852	851	1
5	7	1	−1191	−1327	136	1	−10	2	−646	−576	−70	4	6	2	−441	−402	−39
5	0	−1	−1273	−1418	145	1	−11	2	1037	1033	4	4	7	2	431	457	−26
5	1	−1	−729	−652	−77	1	−12	2	451	435	16	4	8	2	−954	−1019	65
5	2	−1	−1868	−1848	−20	1	−1	−2	2269	2355	−86	4	0	−2	1242	1218	24
5	4	−1	1180	1173	7	1	−2	−2	1006	1042	−36	4	1	−2	1868	1872	−4
5	6	−1	1119	1155	−36	1	−3	−2	−749	−705	−44	4	2	−2	−954	−898	−56
5	7	−1	−462	−458	−24	1	−4	−2	903	747	156	4	3	−2	277	242	35
5	8	−1	−698	−844	146	1	−5	−2	−1253	−1271	22	4	4	−2	−1088	−1100	12
5	9	−1	−349	−362	13	1	−7	−2	1406	1280	126	4	5	−2	−1129	−1223	94
5	−1	1	−1653	−1705	52	1	−8	−2	770	723	47	4	6	−2	420	301	119
5	−2	1	−718	−721	3	1	−10	−2	636	560	76	4	7	−2	225	224	1
5	−3	1	523	493	30	1	−11	−2	−1037	−1042	5	4	8	−2	215	244	−29
5	−5	1	770	808	−38	1	−12	−2	277	258	19	4	9	−2	616	741	−125
5	−6	1	605	591	14	2	0	2	1078	974	104	4	10	−2	−431	−438	7
5	−7	1	−554	−614	60	2	1	2	1689	1630	59	4	−1	2	564	468	96
5	−9	1	−349	−331	−18	2	2	2	−954	−855	−99	4	−2	2	266	−234	−32
5	−1	−1	−1078	−1026	−52	2	3	2	1714	1665	49	4	−3	2	544	494	50
5	−2	−1	1704	1785	−81	2	4	2	−2063	−2088	25	4	−4	2	1047	1031	16
5	−3	−1	−410	−336	−74	2	5	2	−1601	−1638	37	4	−5	2	−308	−284	−24
5	−4	−1	1119	1074	45	2	6	2	−420	−292	−128	4	−6	2	−451	−426	−25
5	−6	−1	−1180	−1196	18	2	7	2	−1262	−1245	−17	4	−8	2	−718	−780	62
5	−7	−1	−533	−549	16	2	8	2	554	507	47	4	−9	2	225	268	−43
5	−8	−1	−462	−461	−21	2	9	2	965	1035	−70	4	−1	−2	−410	−341	−69
5	−9	−1	−595	−609	14	2	10	2	−410	−408	−2	4	−2	−2	852	837	15
5	−10	−1	565	567	18	2	11	2	544	554	−10	4	−3	−2	−1622	−1696	76
6	0	1	903	808	95	2	1	−2	−2946	−2954	8	4	−4	−2	−1283	−1251	−32
6	1	1	1139	1055	84	2	2	−2	1119	991	128	4	−5	−2	400	326	74
6	3	1	657	595	62	2	3	−2	−1191	−1016	−175	4	−6	−2	−718	−689	−29
6	4	1	−503	−503	0	2	4	−2	1273	1106	167	4	−7	−2	1016	1051	−35
6	5	1	−492	−585	93	2	5	−2	1858	1862	−4	4	−8	−2	893	826	67
6	6	1	267	235	32	2	6	−2	533	468	65	4	−9	−2	−205	−194	−11
6	0	−1	−862	−807	−55	2	9	−2	−1037	−1027	−10	4	−10	−2	316	317	1
6	1	−1	308	305	3	2	10	−2	318	273	45	4	−11	−2	−390	−365	−25
6	2	−1	749	786	−37	2	11	−2	379	351	28	5	1	2	−390	−333	−57
6	4	−1	451	425	26	2	12	−2	225	236	−11	5	2	2	1416	1489	−73
6	5	−1	−595	−561	−24	2	−1	2	−1458	−1447	−11	5	3	2	328	316	12
6	6	−1	−944	−1026	82	2	−2	2	−677	−680	3	5	5	2	236	224	12
6	−1	1	−544	−541	−3	2	−3	2	−1150	−1129	−21	5	6	2	−523	−608	85
6	−3	1	−585	−579	−6	2	−4	2	−1714	−1741	27	5	0	−2	−1180	−1196	16
6	−4	1	−831	−888	57	2	−5	2	954	960	−6	5	1	−2	−297	−285	−12
6	−5	1	934	966	−32	2	−7	2	266	223	43	5	2	−2	−995	−939	−56
6	−7	1	513	735	−222	2	−8	2	277	269	8	5	3	−2	−611	−765	46
6	−1	−1	−462	−450	−12	2	−9	2	−687	−673	−14	5	4	−2	718	649	69
6	−2	−1	−390	−415	25	2	−10	2	−790	−771	−19	5	5	−2	616	564	52
6	−3	−1	−831	−846	15	2	−1	−2	1622	1550	72	5	7	−2	595	720	−125
6	−4	−1	995	976	19	2	−2	−2	503	413	90	5	8	−2	−883	−1054	171
6	−7	−1	277	303	−26	2	−3	−2	2905	3011	−106	5	9	−2	−308	−467	159
6	−8	−1	−800	−907	107	2	−4	−2	1612	1531	81	5	−1	2	−266	−240	−26
7	0	−1	759	794	−35	2	−5	−2	−1108	−1059	−49	5	−2	2	−1304	−1333	29
7	2	−1	626	626	0	2	−6	−2	975	938	37	5	−3	2	410	357	53
7	3	−1	−759	−663	−96	2	−7	−2	−1766	−1780	14	5	−4	2	605	543	62
7	4	−1	−708	−782	74	2	−8	−2	−215	−162	−53	5	−5	2	256	242	14
7	−1	−1	862	834	28	2	−9	−2	718	666	52	5	−6	2	1375	1408	−33
7	−2	−1	−585	−640	55	2	−10	−2	195	177	18	5	−7	2	−174	−164	−10
7	−4	−1	−595	−614	19	2	−11	−2	698	739	−41	5	−1	−2	718	643	75
7	−5	−1	−544	−615	71	2	−12	−2	636	634	2	5	−2	−2	564	443	121
0	0	2	−616	−514	−102	3	0	2	277	178	99	5	−5	−2	−462	−416	−44
0	1	2	−2495	−2465	−30	3	1	2	1314	1281	33	5	−6	−2	−1078	−1201	123
0	2	2	184	169	15	3	2	2	−1673	−1697	24	5	−7	−2	359	377	−18
0	3	2	−2905	−2998	93	3	3	2	−770	−725	−45	5	−8	−2	−410	−422	12
0	4	2	677	529	148	3	4	2	−472	−390	−82	5	−9	−2	256	243	13
0	5	2	1776	1779	−3	3	5	2	−739	−750	11	5	−10	−2	492	593	−101
0	7	2	1930	1898	32	3	6	2	533	541	−8	6	0	2	1067	1286	−219
0	9	2	−1067	−1059	−8	3	7	2	800	834	−34	6	0	−2	−1262	−1315	53
0	11	2	−790	−812	22	3	8	2	−564	−549	−15	6	1	−2	−667	−645	−22
0	12	2	−123	−111	−12	3	9	2	297	307	−10	6	2	−2	605	591	14
0	−1	2	2566	2679	−113	3	10	2	−554	−566	32	6	4	−2	451	434	17
0	−2	2	472	380	92	3	0	−2	1139	1086	53	6	5	−2	441	458	−17
0	−3	2	1653	1478	175	3	1	−2	595	476	119	6	6	−2	−852	−880	28
0	−4	2	924	807	117	3	2	−2	1026	939	87	6	7	−2	−236	−233	−3
0	−5	2	−1796	−1725	−71	3	3	−2	2002	1995	7	6	−2	2	605	481	124
0	−7	2	−441	−325	−116	3	4	−2	−585	−536	−49	6	−2	−2	−1314	−1327	13
0	−9	2	1037	955	82	3	5	−2	−739	−645	−94	6	−3	−2	544	531	13
0	−10	2	533	496	37	3	6	−2	−441	−359	−82	6	−4	−2	554	514	40
0	−11	2	−308	−317	9	3	7	−2	−1612	−1610	−2	6	−6	−2	431	382	49
0	−12	2	236	236	0	3	8	−2	636	601	35	6	−7	−2	−297	−319	22
1	0	2	−1150	−1128	−22	3	9	−2	595	583	12	6	−8	−2	−770	−805	35
1	1	2	−2587	−2308	−279	3	10	−2	420	430	−10	7	0	−2	554	466	88
1	2	2	174	114	60	3	11	−2	975	1027	−52	7	1	−2	143	115	28
1	3	2	965	815	150	3	−1	2	698	544	154	7	−2	−2	−687	−667	−20
1	4	2	−533	−417	−116	3	−2	2	1252	1149	103	7	−4	−2	−523	−543	20
1	5	2	1252	1189	63	3	−3	2	−1509	−1455	−54	0	0	3	−1314	−1276	−38
1	6	2	−755	−712	−47	3	−4	2	−1293	−1298	5	0	1	3	−359	−325	−34
1	7	2	−1365	−1255	−110	3	−5	2	−564	−460	−104	0	2	3	−1016	−1035	19
1	9	2	−626	−603	−23	3	−6	2	−1725	−1810	85	0	3	3	−1283	−1252	−31
1	11	2	995	1030	−35	3	−7	2	1160	1077	83	0	4	3	1026	993	33
1	12	2	−462	−449	−13	3	−8	2	338	343	−5	0	7	3	472	425	47
1	0	−2	863	778	105	3	−9	2	390	390	0	0	8	3	−800	−792	−8
1	1	−2	−554	−325	−229	3	−10	2	657	590	67	0	9	3	−636	−608	−28

TABLE 3. (*Continued.*)

h	*k*	*l*	F_o	F_c	F_o-F_c	*h*	*k*	*l*	F_o	F_c	F_o-F_c	*h*	*k*	*l*	F_o	F_c	F_o-F_c
0	10	3	205	176	29	2	-6	3	913	1037	-124	0	-6	4	-349	-334	-15
0	-1	3	924	862	62	2	-8	3	1006	1047	-41	1	0	4	-1119	-1179	60
0	-2	3	1560	1504	56	2	-1	3	441	308	133	1	1	4	667	695	-28
0	-3	3	-236	-193	-43	2	-2	3	657	613	44	1	2	4	533	469	64
0	-4	3	1211	1149	62	2	-3	3	1632	1722	-90	1	5	4	-349	-386	37
0	-5	3	-1088	-1063	-25	2	-4	3	-513	-475	-38	1	6	4	-720	-836	116
0	-6	3	-1386	-1407	21	2	-7	3	-636	-605	-31	1	0	-4	1006	1016	-10
0	-8	3	-672	-659	-13	2	-8	3	420	398	22	1	2	-4	616	610	6
0	-9	3	431	446	-15	2	-9	3	708	705	3	1	4	-4	-1139	-1220	81
0	-10	3	841	792	49	3	2	3	-1396	-1541	145	1	6	-4	-575	-619	44
1	0	3	-369	-392	23	3	6	3	1160	1412	-232	1	8	-4	718	716	2
1	1	3	-1160	-1087	-73	3	0	-3	-369	-357	-12	1	-2	4	-1057	-1143	86
1	2	3	1550	1528	22	3	2	-3	-523	-466	-57	1	-3	4	-739	-747	8
1	3	3	-225	-197	-28	3	3	-3	1663	1742	-79	1	-4	4	503	417	86
1	6	3	-1540	-1688	148	3	4	-3	503	466	37	1	-6	4	379	330	49
1	7	3	-677	-615	-62	3	5	-3	359	284	75	1	-7	4	595	632	-37
1	9	3	-770	-773	3	3	8	-3	-390	-401	11	1	-2	-4	-831	-913	82
1	10	3	841	943	-102	3	9	-3	533	517	16	1	-4	-4	-662	-737	75
1	0	-3	646	498	148	3	-2	3	1098	1190	-92	1	-6	-4	513	486	27
1	1	-3	739	643	96	3	-4	3	-482	-405	-77	2	0	4	564	471	93
1	2	-3	1283	1136	147	3	-6	3	-616	-569	-27	2	2	4	266	182	84
1	3	-3	-524	-761	-163	3	-8	3	667	645	22	2	3	4	-492	-540	48
1	4	-3	-852	-762	-90	3	-1	-3	-1334	-1271	-63	2	4	4	-735	-812	73
1	6	-3	-718	-596	-122	3	-2	-3	733	657	82	2	5	4	451	480	-29
1	7	-3	872	783	89	3	-3	-3	913	833	80	2	0	-4	1026	1004	22
1	8	-3	698	652	46	3	-5	-3	1817	2022	-205	2	2	-4	-595	-559	-36
1	-1	3	-729	-724	-5	3	-6	-3	-492	-461	-31	2	6	-4	790	860	-70
1	-2	3	-1509	-1462	-47	3	-9	-3	-698	-674	-24	2	-1	4	595	637	-42
1	-4	3	749	655	94	4	0	3	-1334	-1240	-94	2	-4	4	-523	-472	-51
1	-5	3	-431	-349	-82	4	1	3	472	367	105	2	-5	4	-482	-460	-2
1	-6	3	800	710	90	4	2	3	-544	-386	-158	2	-6	4	215	246	-31
1	-8	3	-759	-795	36	4	3	3	544	479	65	2	-2	-4	760	820	-40
1	-1	-3	1601	1580	21	4	4	3	1016	1034	-18	2	-4	-4	-883	-917	34
1	-2	-3	-1642	-1618	-24	4	1	-3	1406	1477	-71	2	-6	-4	-452	-478	-14
1	-3	-3	-492	-454	-38	4	3	-3	-554	-481	-73	2	-8	-4	739	802	-63
1	-4	-3	-575	-431	-144	4	5	-3	-1006	-1128	122	3	0	4	472	460	12
1	-5	-3	-1365	-1317	-48	4	6	-3	-277	-319	42	3	1	4	-739	-863	124
1	-6	-3	1273	1235	38	4	-2	3	595	584	11	3	2	4	-308	-356	48
1	-7	-3	462	454	8	4	-4	3	1201	1192	9	3	0	-4	-770	-675	-95
1	-9	-3	554	868	66	4	-5	3	646	630	16	3	3	-4	420	307	113
1	-10	-3	-667	-675	-12	4	-6	3	-379	-392	13	3	4	-4	1232	1376	-144
1	-11	-3	-277	-320	43	4	-1	-3	667	541	146	3	6	-4	513	518	-5
2	0	3	1622	1593	29	4	-3	-3	-611	-639	28	3	7	-4	-266	-269	3
2	1	3	-431	-361	-70	4	-5	-3	492	356	136	3	-2	4	564	577	-13
2	2	3	893	843	50	5	3	-3	-1211	-1220	9	3	-1	-4	-420	-379	-41
2	4	3	-1170	-1282	112	5	-1	-3	1160	1262	-102	3	-2	-4	667	745	-78
2	5	3	-462	-382	-80	5	-3	-3	-205	-82	-123	3	-4	-4	611	512	-101
2	7	3	-554	-509	-45	5	-5	-3	-1129	-1227	98	3	-5	-4	410	349	61
2	8	3	831	873	-42	6	1	-3	-903	-970	67	4	1	-4	575	464	111
2	0	-3	575	473	102	6	5	-3	420	410	10	4	2	-4	611	677	-66
2	1	-3	-1108	-1075	-33	6	-1	-3	-595	-564	-31	4	4	-4	462	439	23
2	2	-3	-1191	-1132	-59	6	-3	-3	410	356	54	4	6	-4	-338	-307	-31
2	3	-3	1037	870	167	6	-5	-3	-328	-273	-55	4	-3	-4	-585	-512	-73
2	4	-3	-605	-494	-111	0	0	4	-1273	-1254	-19	4	-4	-4	862	900	-38
2	5	-3	1766	1874	-108	0	1	4	205	169	36	4	-6	-4	646	705	-59
2	6	-3	1078	1020	58	0	2	4	-862	-904	42	5	0	-4	739	660	79
2	9	-3	-626	-623	-3	0	3	4	318	275	43	5	3	-4	-472	-431	-41
2	10	-3	-780	-747	-33	0	4	4	749	736	13	5	4	-4	-523	-567	44
2	-1	3	-646	-573	-73	0	5	4	-308	-305	-3	5	-1	-4	544	517	27
2	-2	3	-1242	-1154	-88	0	-1	4	-379	-367	-12	1	-1	-5	-626	-742	116
2	-3	3	-626	-500	-126	0	-2	4	308	275	33	2	1	-5	349	421	-72
2	-4	3	-1427	-1492	65	0	-5	4	256	286	-30	2	2	-5	-410	-523	113
2	-5	3	-420	-359	-61	0	-6	4	-683	-689	6	2	-2	-5	236	441	-205

TABLE 4.

Bond lengths (Å) and angles.

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C–S	1·665 (5)	1·633 (5)	S–C–N	125·4 (4)	124·6 (4)
C–N	1·336 (7)	1·311 (7)	S–C–C.....	119·6 (3)	120·5 (4)
C–C	1·536 (14)	1·538 (14)	N–C–C	115·0 (4)	114·8 (4)

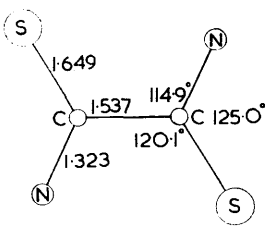

FIG. 1. Mean molecular dimensions in dithio-oxamide.

The mean C–S bond length is considerably shorter than that in thioacetamide [9] (which is a similar structure in that there are two independent molecules in the unit cell), in

[9] Truter, *J.*, 1960, 997.

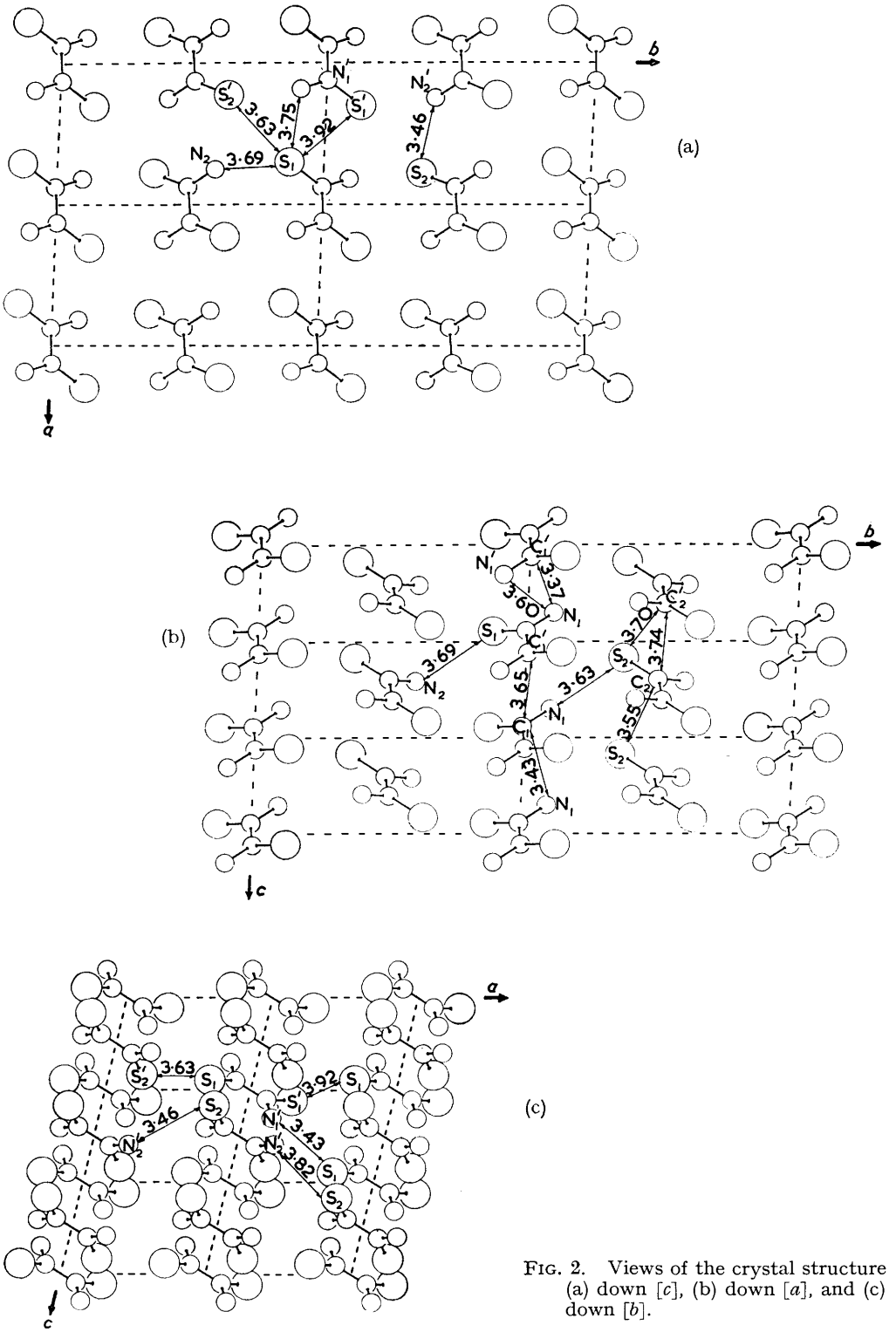

FIG. 2. Views of the crystal structure (a) down [*c*], (b) down [*a*], and (c) down [*b*].

thiourea,[10] or in ethylenethiourea.[11] On the other hand, the mean C–N length agrees well with that in the above three molecules. The C–C length is in good agreement with that in oxamide,[12] and indeed with that in a number of isoelectronic molecules that have been listed and discussed.[13] It is still not clear why these molecules should be planar and yet have a central bond with the length of a single bond.

Both molecules are accurately planar. The equations for the weighted least-squares planes, in terms of the orthogonal axes, are:

$$\text{Molecule 1} \quad -0{\cdot}51175X' + 0{\cdot}40512Y' + 0{\cdot}75762Z' = 0;$$
$$\text{Molecule 2} \quad +0{\cdot}47891X' + 0{\cdot}37663Y' - 0{\cdot}79297Z' = +0{\cdot}26365.$$

No atom departs significantly from its plane, the largest deviation for molecule 1 being −0·007 Å for C(1), and for molecule 2 being −0·004 Å for C(2). The molecular planes make an angle of 46·1° with each other. The angles that the molecular planes make with the three orthogonal axes are given in Table 5.

TABLE 5.

Orientation of the two independent molecules with respect to the three orthogonal axes.

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
[*a*′]	59·2°	61·4°	[*c*′]	40·8°	37·5°
[*b*] = [*b*′].....	66·1	67·9			

The molecules are separated by the [*c*] translation, 3·936 Å. There are seventeen van der Waals contacts less than this. The two shortest, 3·371 and 3·431 Å, are between carbon and nitrogen atoms, in each case the nitrogen atom involved being that in molecule 1. The next shortest contacts, 3·432 and 3·456 Å, are between nitrogen and sulphur atoms. There is thus some indication of the presence of N–H · · · S hydrogen bonds, though the evidence is not as convincing as in thioacetamide,[9] where the shortest contact distance, 3·396 Å, is between a nitrogen and a sulphur atom. The shortest contact between two sulphur atoms is 3·629 Å. Fig. 2, which shows views of the crystal structure down the three principal triclinic axes, includes some of the shorter van der Waals contacts.

Most of the early work was carried out at the University of Leeds by Dr. P. Markey under the guidance of Sir Gordon Cox, F.R.S., and Professor G. A. Jeffrey. I thank these colleagues, and am also indebted to the Ministry of Education, Imperial Chemical Industries Limited, and the Royal Society for supporting grants, and to the Staff of the Manchester University Computing Laboratory for the provision of facilities.

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[*Received, April 28th,* 1964.]

[10] Kunchur and Truter, *J.*, 1958, 2551.
[11] Wheatley, *Acta Cryst.*, 1953, **6**, 369.
[12] Averst and Duke, *Acta Cryst.*, 1954, **7**, 588.
[13] Wheatley, *J.*, 1956, 868.