Rh_{II}–$2Te_I$	2·76 Å	Te_{II}–$1Rh_I$	2·64 Å
–$1Te_{II}$	2·61	–$2Rh_{II}$	2·61
–$2Te_{II}$	2·63	–$4Rh_{II}$	2·63

–$1Rh_I$	2·82
–$1Rh_I$	2·86
–$1Rh_{II}$	2·91
–$2Rh_{II}$	3·05

Table 3. Structure factors

$HK0$	F_c	$\lvert F_o \rvert$	$HK1$	F_c	$\lvert F_o \rvert$
800	45	41	4,11,1	72	79
3,12,0	−21	30	811	40	40
820	58	58	0,13,1	0	3
840	137	120	1,13,1	36	41
4,12,0	49	60	691	−4	7
780	51	51	831	−48	46
6,10,0	121	123	771	−15	13
0,14,0	−26	32	2,13,1	−20	23
1,14,0	5	8	5,11,1	46	46
860	−49	51	851	36	33
2,14,0	101	111	3,13,1	−73	80
5,12,0	−33	33	791	−71	67
920	−30	31	4,13,1	48	48
3,14,0	70	77	911	55	52
940	−5	6	6,11,1	8	6
7,10,0	17	17	871	79	71
880	74	74	931	−15	14
4,14,0	−26	30	0,15,1	120	97
6,12,0	−8	11	1,15,1	−44	41
960	−27	30			
0,16,0	−15	15			

The shortest Te–Te distance in the structure is 3·70 Å.

In the high temperature (CdI_2) and low temperature (pyrite) forms of $RhTe_2$ Geller (1954) reported Rh–6Te = 2·65 and 2·64 Å. Geller gives Rh–6Te = 2·70 Å and Rh–2Rh = 2·83 Å for the high-temperature form (NiAs) of RhTe.

References

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The Crystal Structure of Benzotrifuroxan (Hexanitrosobenzene)*

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The crystal structure of benzotrifuroxan (hexanitrosobenzene) has been refined by full-matrix least-squares computations on all positional and thermal parameters to a final weighted R index of 0·040 for 606 reflections of observable intensity. The unit cell is orthorhombic ($a = 6·923$, $b = 19·516$, $c = 6·518$ Å), space group $Pna2_1$, with four molecules per unit cell.

The molecule is essentially planar, and the six nitroso substituents have formed three furoxan rings.

Introduction

There has been considerable interest in the configuration of benzofuroxans. Kaufman & Pickard (1959) cover the classical aspects of this interest in their review article. More recently Harris, Katritzky, Øksne, Bailey & Patterson (1963) have proven the benzofuroxan configuration of this type of compound in solution. Previous X-ray work on this problem consists in two preliminary and somewhat contradictory studies by Hulme (1962) and Gol'der, Todres-Selektor & Bognadov (1961), and work by Britton & Noland (1962) on the structure of 5-chlorobenzofurazan-1-oxide. Britton & Noland found that this compound has the furoxan structure, but their work leaves unsettled some of the important details of the structure.

In this paper we report the results of a study whose purpose was to elucidate the structure of benzotrifuroxan in the solid state. In particular, we were concerned with the relative importance of the nitroso and furoxan configurations in this symmetric compound, and with the pertinent bond angles and interatomic distances.

Benzotrifuroxan is, incidentally, a powerful and relatively sensitive explosive.

Experimental

A sample of benzotrifuroxan was prepared in this Laboratory following the method of Turek (1931). A single crystal suitable for collection of the X-ray intensity data was grown on its mounting fiber by recrystallization from acetone. The longest internal dimension of this crystal was 0·340 mm. The crystal was aligned and preliminary unit-cell dimensions and space group ex-

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tinctions were determined with precession photographs. The crystal was then transferred to a carefully aligned General Electric Company single-crystal orienter (SCO) equipped with a scintillation counter and a molybdenum X-ray tube.

Cell dimensions were determined from a least-squares fit of 23 2θ (λ Mo $K\alpha_1 = 0.70926$ Å) values, greater than 24°, for general hkl reflections which were measured on the SCO at 21 °C. This least-squares fit gives $a = 6.9234 \pm 0.0009$, $b = 19.5158 \pm 0.0012$, $c = 6.5180 \pm 0.0013$ Å for the orthorhombic unit cell. There are four molecules in the unit cell, and the calculated density of 1.901 g.cm^{-3} compares reasonably with the measured density of 1.87 g.cm^{-3}.

The crystal was mounted with its c axis coincident with the φ axis of the SCO. Background corrections were made by the balanced filter technique. Reflections within a sphere limited by $2\theta = 50°$ were examined by the stationary-counter stationary-crystal technique. Within the quarter of the sphere counted, 1605 space-group-allowed reflections were examined. Of the 853 unique reflections in this set, 606 were strong enough to be observed; i.e. $I - Bkgd > 2.5\sqrt{I + Bkgd}$.

Computational details

Lorentz and polarization corrections were applied. Absorption corrections were made assuming the crystal was box-shaped with sides of lengths 0.145, 0.214, and 0.235 mm (absorption coefficient = 1.87 cm^{-1}). The maximum error introduced by this approximation to the true crystal (22 faces) was less than 0.05%. The program described by Larson, Cromer & Roof (1964) was used for these corrections. Equivalent F^2 values were averaged and the observed F was taken as the square root of this average. The average agreement of equivalent reflections was estimated by forming an index

$$\Sigma |F^2 - \overline{F^2}|/\Sigma \overline{F^2},$$

where the summation was taken over all reflections which were observed more than once. This index was 0.054. A similar quantity,

$$\Sigma |F - \overline{F^2}^{\frac{1}{2}}|/\Sigma \overline{F^2}^{\frac{1}{2}},$$

based on F, was 0.032.

All least-squares calculations were made with the use of the full matrix. The least-squares parameters included, in addition to atomic position and thermal parameters, one scale factor and one parameter to allow for secondary extinction. The secondary extinction parameter was found to be negligible and was set equal to zero in the later stages of the refinement. The quantity minimized was $\Sigma w(F_o - F_c^*)^2$, where

$$|F_c^*| = |F_c|/k\left\{1 + g\left[\frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2}\right] \text{Lp} |F_c|^2\right\}^{\frac{1}{4}}$$

in which k = scale factor, g = extinction parameter (Zachariasen, 1963), Lp = Lorentz and polarization fac-

tors, and F_c is the calculated structure factor, and where $w = w_E/(|F_o| + 0.02|F_o|^2)$ for all observed reflections and $w = 0.0$ for unobserved reflections. The term w_E is the weight based on counting statistics as described by Evans (1961). Anisotropic thermal parameters were in the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})]$. The R index is defined as $(\Sigma w||F_o| - |F_c^*||/\Sigma w|F_o|)$.

The estimated standard deviations were calculated from

$$\sigma_j = \sqrt{a^{jj}\left[\frac{\Sigma w(|F_o| - |F_c^*|)^2}{m - n}\right]}$$

where m is the number of observed reflections, n is the number of parameters, and a^{jj} is the jj element of the inverse matrix. The atomic scattering factors used are those given in International Tables for X-Ray Crystallography (1962).

All calculations were performed on IBM 7094 or 7030 computers, with codes written by the authors unless otherwise indicated.

Determination and refinement of the structure

The space group is not uniquely determined by systematic extinctions ($0kl$ with ($k + l$) odd, $h0l$ with h odd) and could be either $Pna2_1$ or $Pnam$. A three-dimensional sharpened Patterson map was computed. Inspection of the Patterson map and statistical tests of the data (Howells, Phillips & Rogers, 1950; Ramachandran & Srinivasan, 1959) indicated the proper space group to be $Pna2_1$. The orientation of a molecule could be derived from the Patterson map; however, the x and y coordinates of atoms were not obvious.

Since the general position set for space group $Pna2_1$ is fourfold and because so much was known about the geometry of the molecule, the problem seemed ideally suited to a vector verification method for determining a trial structure. A code was written which would start with a fixed array of points and then rotate and translate this array into any of its possible orientations in the unit cell. The symmetry related points were generated and the value of the sharpened Patterson map at all interpoint vectors was determined. Scaling of the values for the assumed atomic numbers of the atoms in the vectors, and selection of the lowest value determined from an entire set of vectors, yielded a number indicating the consistency of the model with the Patterson map. This procedure amounts to calculating the value of the minimum function (Buerger, 1959) at each 'atom site' and then selecting the lowest of these values as the index of correctness of the postulated structure.

A search was conducted for likely locations for a benzene group. After many possible benzene group positions were found, nitrogen atoms were added at 1.4 Å from the carbon atoms and several possible trial structures were obtained.

Close inspection of these trial structures revealed that they were all the same except for choice of origin or polar direction in the unit cell.

One set of carbon and nitrogen positions was used to calculate an observed Fourier map. The extra peaks on this map determined the trial positions for the oxygen atoms in the least-squares refinement. With the assumption of isotropic atoms the problem converged rapidly to an R index of 0·10. All atoms were then allowed to become anisotropic, and the refinement continued until all $\Delta\xi_i/\sigma(\xi_i)$ were $< 1\cdot9 \times 10^{-2}$ for all parameters ξ. The final value of R was 0·040.

The final least-squares parameters and their standard deviations are given in Table 1 and the corresponding values of $10 \, k|F_o|$, $10 \, k|F_c^*|$, and α are given

in Table 2. The standard deviation of the electron density (σ_ρ) in the structure is estimated to be $4\cdot73 \times 10^{-2}$ e.Å^{-3} by Cruickshank's (1949) formula. Observed and difference Fourier maps of the final structure were calculated. The peaks and valleys of the difference map indicated no significant errors in the structure.

Detailed description of the structure

Interatomic distances before correction for thermal motion are given in Table 3. The closest intermolecular distance is from N(1) to O(5') of the molecule at $z+1$, which is $2\cdot997 \pm 0\cdot006$ Å. Intramolecular bond angles are given in Fig. 1 (standard deviations for these angles range from 0·4 to 0·6 degrees). Standard deviations for
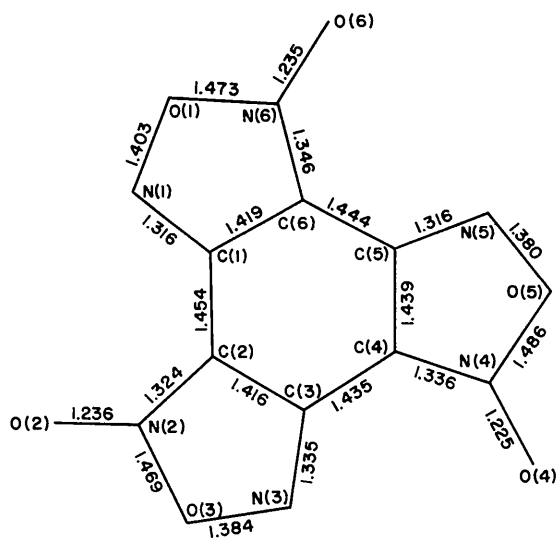

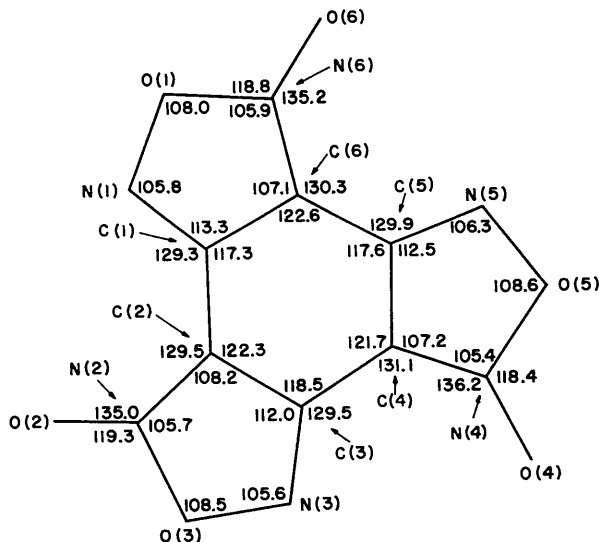Fig. 1. Intramolecular bond lengths (Å).

Fig. 2. Intramolecular bond angles (°).

Table 1. *The final least-squares parameters and their estimated standard deviations for benzotrifuroxane*

The standard deviations apply to the rightmost digits of the least-squares parameters.
The anisotropic temperature factor is of the form: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$; and B is $\frac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$ for an anisotropic atom (Hamilton, 1959).

Atom	x	y	z	$B_{11} \times 10^4$	$B_{22} \times 10^5$	$B_{33} \times 10^4$	$B_{12} \times 10^5$	$B_{13} \times 10^4$	$B_{23} \times 10^4$	$B(\text{Å})^2$
C(1)	0·4165 ± 8	0·0995 ± 2	0	217 ± 13	229 ± 16	245 ± 17	−250 ± 82	−1 ± 28	−10 ± 9	3·94
C(2)	0·6009 ± 8	0·0743 ± 2	−0·0691 ± 13	186 ± 12	223 ± 15	282 ± 17	51 ± 77	−77 ± 27	−8 ± 10	3·92
C(3)	0·6832 ± 7	0·0950 ± 3	−0·2554 ± 14	175 ± 12	235 ± 16	301 ± 18	−13 ± 79	12 ± 28	−24 ± 11	4·02
C(4)	0·5782 ± 7	0·1413 ± 3	−0·3817 ± 12	201 ± 14	249 ± 16	221 ± 17	−198 ± 79	64 ± 26	−18 ± 9	3·80
C(5)	0·3975 ± 7	0·1693 ± 2	−0·3187 ± 13	207 ± 13	210 ± 16	236 ± 17	−40 ± 75	−15 ± 27	−8 ± 9	3·73
C(6)	0·3216 ± 7	0·1475 ± 2	−0·1255 ± 13	171 ± 12	229 ± 16	272 ± 17	21 ± 78	5 ± 27	−36 ± 9	3·79
N(1)	0·3219 ± 6	0·0851 ± 2	0·1677 ± 11	223 ± 11	343 ± 17	275 ± 15	−83 ± 73	40 ± 26	12 ± 10	4·72
N(2)	0·7216 ± 7	0·0317 ± 2	0·0216 ± 12	210 ± 12	275 ± 16	326 ± 18	−34 ± 71	−29 ± 26	6 ± 9	4·58
N(3)	0·8558 ± 6	0·0676 ± 3	−0·2843 ± 13	218 ± 12	335 ± 17	363 ± 19	6 ± 68	57 ± 29	−34 ± 11	5·15
N(4)	0·6153 ± 7	0·1657 ± 2	−0·5680 ± 12	267 ± 13	245 ± 14	260 ± 16	−262 ± 76	26 ± 27	−16 ± 8	4·42
N(5)	0·3245 ± 7	0·2106 ± 2	−0·4545 ± 12	276 ± 13	311 ± 16	267 ± 16	207 ± 80	−13 ± 27	13 ± 9	4·85
N(6)	0·1588 ± 7	0·1653 ± 2	−0·0291 ± 13	199 ± 11	339 ± 16	301 ± 16	−7 ± 76	20 ± 24	−20 ± 10	4·70
O(1)	0·1548 ± 5	0·1252 ± 2	0·1610 ± 12	214 ± 10	409 ± 15	296 ± 13	28 ± 61	82 ± 20	4 ± 8	5·12
O(2)	0·7192 ± 6	−0·0014 ± 2	0·1787 ± 13	277 ± 11	389 ± 15	388 ± 14	180 ± 68	−61 ± 25	89 ± 9	5·95
O(3)	0·8896 ± 5	0·0274 ± 2	−0·1137 ± 12	208 ± 9	330 ± 12	379 ± 15	224 ± 57	−28 ± 25	−6 ± 9	5·15
O(4)	0·7412 ± 6	0·1591 ± 2	−0·6934 ± 12	298 ± 10	402 ± 15	277 ± 14	−344 ± 67	206 ± 23	−34 ± 8	5·51
O(5)	0·4533 ± 6	0·2122 ± 2	−0·6154 ± 11	301 ± 11	330 ± 13	279 ± 13	104 ± 63	1 ± 24	9 ± 8	5·18
O(6)	0·0262 ± 6	0·2035 ± 2	−0·0656 ± 12	247 ± 10	405 ± 14	437 ± 17	722 ± 64	15 ± 23	18 ± 10	6·11

these distances and bond angles were computed using the entire variance–covariance matrix. Examination of Table 3 and Figs. 1 and 2 clearly indicates the benzotrifuroxan structure as opposed to any other of the possible configurations.

The atomic positional parameters were transformed into an isometric set and the plane of the molecule was determined to be $0{\cdot}46634X+0{\cdot}76605Y+0{\cdot}44237Z-2{\cdot}86851=0$. The distances of the atoms from this plane are given in Table 4.

The anisotropic thermal parameters were transformed to obtain the axes of the ellipsoids of thermal vibration and the directions of these axes with respect to the crystallographic axes. These results are presented in Table 5. The standard deviations were computed using the entire variance–covariance matrix.

Rigid body calculations were carried out for the following groups of atoms: (1) the benzene ring, (2) all of the carbon and nitrogen atoms, and (3) the benzotrifurazan ring system. The method of Cruickshank (1956*a*) was employed using a code provided by Trueblood (1963). The center of mass of the rigid body was taken as the unweighted average of the atomic positions. Oxygen atoms (2), (4), and (6) were clearly eliminated from the rigid body by examination of their ellipsoids of thermal vibration. Examination of the thermal and oscillatory motions from the three rigid body calculations showed that the benzene ring was the only group which had reasonable rigid body motions.

The rigid body calculations are strictly valid only when the whole molecule may be regarded as a rigid

Table 2. *Observed and calculated magnitudes of the structure factors for benzotrifuroxan*

The column headings are k, $10k|F_o|$, $10kF_c$ (see text), and α. A minus sign preceding $10k|F_o|$ means 'less than'.

k	$10k\|F_o\|$	$10kF_c$	α
H= 0		L= 0	
2	56	55	360
4	616	600	180
6	604	601	360
8	225	223	180
10	129	122	360
12	166	162	360
14	192	193	360
16	274	265	180
18	-36	0	0
20	-32	9	180
22	60	53	180
H= 0		L= 1	
1	135	142	41
3	857	909	73
5	433	432	51
7	193	194	0
9	93	95	114
11	155	150	111
13	152	163	80
15	43	43	350
17	65	70	56
19	74	74	251
21	-31	31	297
H= 0		L= 2	
0	247	261	316
2	510	541	130
4	304	321	321
6	257	257	293
8	342	339	118
10	110	114	72
12	196	199	169
14	52	56	170
16	178	181	128
18	-31	28	171
20	-30	11	214
22	78	79	122
H= 0		L= 3	
1	291	292	58
3	43	43	199
5	100	103	218
7	278	273	60
9	126	125	346
11	111	105	296
13	106	111	125
15	83	84	9
17	101	108	318
19	-33	41	140
21	-35	20	55
H= 0		L= 4	
0	483	477	254
2	124	127	309
4	87	87	94
6	140	132	185
8	130	123	152
10	103	104	307
12	165	161	302
14	117	121	194
16	56	61	245
18	46	56	325
H= 0		L= 5	
1	152	149	10
3	37	36	353
5	72	71	2
7	150	148	214
8	-30	0	292
9	179	171	179
11	87	89	62
13	62	68	178
15	-31	20	18
17	-35	28	292
H= 0		L= 6	
0	71	80	39
2	67	56	39
4	122	120	115
6	49	52	315
8	56	57	353
10	45	52	83
12	53	56	258
14	-35	30	156
H= 0		L= 7	
1	58	56	91
3	120	109	156
5	38	39	290
7	-36	30	14
9	55	57	170
H= 1		L= 0	
1	381	389	180
2	90	53	180
3	551	557	360
4	693	686	360
5	148	146	0
6	260	258	360
7	71	74	0
8	448	444	360
9	-21	24	180
10	94	53	180
11	117	119	180
12	30	25	360
13	226	224	180
14	105	103	360
15	74	78	360
16	-27	14	180
17	54	54	0
18	-31	26	360
19	65	59	180
20	36	33	180
21	-31	11	180
22	-32	3	180
23	40	39	180
H= 1		L= 1	
1	203	207	181
2	411	417	102
3	901	894	255
4	868	864	274
5	535	518	327
6	617	622	37
7	609	603	29
8	217	206	126
9	290	284	234
10	190	184	90
11	69	70	51
12	43	41	6
13	183	180	48
14	-27	27	270
15	68	66	221
16	32	31	33
17	69	65	33
18	38	38	248
19	111	105	25
20	57	62	64
21	37	40	100
22	-36	44	252
H= 1		L= 2	
1	175	178	221
2	392	401	234
3	146	153	239
4	223	225	341
5	283	290	323
6	22	20	284
7	161	155	308
8	176	179	352
9	35	32	129
10	111	112	19
11	66	71	326
12	110	104	295
13	60	60	106
14	87	87	250
15	47	49	119
16	-28	18	90
17	38	42	94
18	72	72	323
19	-32	23	79
20	52	51	215
21	-35	30	287
22	59	68	130
H= 1		L= 3	
1	195	159	250
2	172	163	296
3	262	259	127
4	257	253	187
5	241	254	97
6	221	233	14
7	120	128	141
8	-23	22	254
9	56	56	114
10	125	132	293
11	162	160	87
12	148	150	334
13	-27	7	74
14	39	41	2
15	45	54	227
16	54	56	157
17	94	93	105
18	44	47	182
19	56	58	51
20	-35	28	14
21	-33	10	18
H= 1		L= 4	
1	33	31	152
2	193	187	53
3	157	153	174
4	121	116	127
5	92	96	328
6	107	114	268
7	29	33	125
8	105	112	96
9	96	102	229
10	-26	15	20
11	93	99	128
12	-30	19	102
13	106	110	39
14	34	37	65
15	82	81	325
16	44	38	310
17	-33	32	95
18	-31	8	256
19	-32	7	327
H= 1		L= 5	
1	58	63	52
2	114	111	316
3	107	100	214
4	107	107	190
5	95	100	297
6	78	84	226
7	73	80	256
8	117	123	24
9	33	23	317
10	50	55	260
11	42	49	154
12	-32	23	232
13	44	48	168
14	-31	4	226
15	-32	25	241
16	38	36	223
17	-32	15	203
H= 1		L= 6	
1	-29	18	108
2	126	121	205
3	66	61	119
4	108	108	109
5	64	62	261
6	39	49	38
7	39	41	66
8	-33	29	4
9	36	41	255
10	45	50	19
11	-33	30	192
12	54	56	113
13	-34	24	28
14	39	36	188
H= 1		L= 7	
1	46	49	11
2	-32	11	300
3	-32	26	218
4	38	33	55
5	71	72	332
6	43	43	175
7	-34	15	352
8	-32	12	5
9	-36	26	114
H= 2		L= 0	
0	559	561	180
1	41	38	180
2	551	556	180
3	58	58	180
4	136	133	0
5	546	560	360
6	255	258	180
7	77	77	360
8	212	213	180
9	138	136	180
10	119	120	0
11	144	145	360
12	206	210	180
13	-24	0	360
14	-26	9	360
15	85	82	0
16	36	39	360
17	-29	17	180
18	-28	8	180
19	-31	17	180
20	-32	11	180
21	-35	30	360
22	-32	9	180
H= 2		L= 1	
0	434	451	155
1	145	147	359
2	306	310	244
3	203	200	312
4	205	199	100
5	218	208	162
6	400	384	191
7	137	131	328
8	185	179	253
9	253	242	293
10	191	194	29
11	91	93	142
12	85	85	273
13	36	42	330
14	116	117	70
15	-28	14	231
16	78	80	129
17	-29	24	43
18	81	78	146
19	-30	6	27
20	67	70	309
21	43	42	108
22	44	52	321
H= 2		L= 2	
0	514	531	312
1	128	133	163
2	76	76	278
3	93	96	208
4	424	407	245
5	94	85	77
6	178	162	111
7	338	316	167
8	68	62	65
9	393	379	273
10	329	332	294
11	366	363	320
12	157	157	40
13	126	122	103
14	81	82	325
15	-29	14	191
16	-30	23	294
17	42	39	240
18	-29	17	346
19	105	107	133
20	38	48	21
21	-32	14	334
H= 2		L= 3	
0	-23	11	70
1	147	145	115
2	41	43	167
3	150	140	351
4	91	94	107
5	106	98	359
6	106	104	163
7	191	184	257
8	126	119	212
9	153	148	255
10	73	75	253
11	64	63	63
12	31	30	337
13	78	79	277
14	117	115	21
15	-32	39	131
16	109	103	320
17	40	33	24
18	74	71	277
19	38	44	206
20	-32	19	161
H= 2		L= 4	
0	186	179	215
1	113	115	107
2	188	186	74
3	67	61	305
4	81	74	188
5	95	98	247
6	64	65	238
7	142	131	186
8	130	128	64
9	38	37	185
10	32	36	96
11	-29	14	119
12	70	73	45
13	83	83	208
14	-30	13	46
15	47	55	176
16	58	64	55
17	-34	30	334
18	-32	5	12
19	-34	18	55
H= 2		L= 5	
0	118	125	73
1	81	81	111
2	41	45	27
3	52	53	197
4	57	56	194
5	89	85	303
6	161	158	85
7	57	54	334
8	41	38	19
9	-30	21	348
10	99	102	270
11	43	44	311
12	-33	30	32
13	36	35	243
14	-33	24	166
15	-33	26	82
16	-32	10	38
H= 2		L= 6	
0	84	91	197
1	156	150	70
2	42	34	258
3	46	55	27
4	-32	17	196
5	43	46	257
6	35	47	169
7	59	53	93
8	-31	20	257
9	71	71	171
10	-31	11	345
11	60	58	218
12	-33	20	91
13	59	66	342
H= 2		L= 7	
0	38	48	219
1	47	52	310
2	43	40	317
3	-34	22	354
4	-32	10	18
5	-32	9	84
6	48	46	102
7	-34	15	267
8	-34	15	131
H= 3		L= 0	
1	197	193	360
2	119	117	180
3	100	98	180
4	305	298	360
5	147	142	0
6	36	39	180
7	126	127	180
8	128	124	360
9	74	70	360
10	64	60	180
11	176	168	360
12	98	101	180
13	68	68	360
14	-28	28	180
15	-30	28	180
16	96	99	360
17	109	107	180
18	91	90	360
19	37	39	360
20	-35	34	180
21	39	44	360
H= 3		L= 1	
1	378	376	161
2	146	142	344
3	128	122	[illegible]
4	299	297	150
5	126	125	177
6	164	161	141
7	182	178	136
8	174	174	238
9	91	88	125
10	167	164	359
11	98	91	10
12	39	40	304
13	83	79	214
14	59	66	224
15	88	92	203
16	83	82	81
17	43	42	350
18	47	51	208
19	-33	36	80
20	43	48	265
21	-37	39	101
H= 3		L= 2	
1	30	27	92
2	76	81	10
3	223	217	91
4	274	263	227
5	195	186	63
6	85	83	204
7	196	189	221
8	197	191	311
9	90	91	73
10	156	142	155
11	176	170	152
12	114	107	236
13	81	78	175
14	61	68	313
15	118	118	328
16	57	65	94
17	-32	15	243
18	52	60	304
19	-31	14	150
20	-33	27	358
H= 3		L= 3	
1	186	182	131
2	104	105	304
3	193	182	247
4	121	111	153
5	73	77	66
6	145	136	334
7	48	50	314
8	146	140	150
9	107	99	234
10	146	140	74
11	57	62	13
12	135	123	135
13	44	39	293
14	109	105	216
15	150	146	262
16	88	86	334
17	78	80	322
18	42	42	87
19	39	49	35
H= 3		L= 4	
1	-27	29	359
2	136	140	214
3	30	34	302
4	139	125	219
5	30	34	359
6	31	31	3
7	-29	31	175
8	117	111	212
9	118	116	1
10	72	67	127
11	51	84	259
12	57	57	156
13	77	74	205
14	77	77	211
15	-31	21	175
16	-32	17	230
17	-33	19	165
H= 3		L= 5	
1	71	66	66
2	73	71	229
3	159	152	112
4	131	123	64
5	47	40	354
6	71	65	26
7	106	104	311
8	146	139	182
9	101	95	69
10	-33	13	223
11	-31	23	146
12	-34	40	36
13	-33	30	285
14	-32	8	117
15	-32	9	76
H= 3		L= 6	
1	-31	16	121
2	80	86	194
3	72	66	332
4	-31	8	78
5	-32	21	20
6	-30	11	340
7	37	40	107
8	46	43	178
9	-31	7	138
10	-35	30	352
11	-32	6	319
H= 3		L= 7	
1	-34	27	79
2	-37	24	160
3	-35	32	181
4	-34	28	235
5	40	33	283
H= 4		L= 0	
0	327	317	180
1	-22	4	360
2	90	90	180
3	52	52	0
4	290	292	360
5	27	29	180
6	84	87	360
7	-25	18	0
8	60	57	0
9	56	59	0
10	109	112	360
11	116	115	360
12	91	91	180
13	165	165	360
14	-31	25	0
15	87	88	180
16	-29	9	360
17	101	98	180
18	-33	20	180
19	-32	15	0
20	62	66	360
H= 4		L= 1	
0	243	248	321
1	137	131	180
2	134	133	233
3	180	175	238
4	56	59	26
5	47	47	192
6	177	181	320
7	176	172	148
8	122	118	318
9	39	45	229
10	50	50	156
11	92	93	9
12	102	104	173
13	33	37	216
14	160	160	31
15	55	60	206
16	53	54	22
17	-31	19	311
18	-31	9	300
19	-33	23	209
20	-33	13	345
H= 4		L= 2	
0	54	58	230
1	91	92	207
2	227	227	78
3	92	90	16
4	172	169	70
5	127	126	293
6	113	116	153
7	36	32	346
8	54	49	155
9	68	69	50
10	-27	16	312
11	45	52	233
12	118	117	146
13	50	51	12
14	34	33	252
15	50	49	253
16	-34	36	325
17	-31	8	192
18	-36	40	151
19	-34	12	127
H= 4		L= 3	
0	224	225	324
1	77	78	50
2	121	125	137
3	30	30	164
4	52	53	121
5	93	93	173
6	70	70	166
7	51	46	58
8	95	96	88
9	104	101	120
10	61	58	335
11	90	84	122
12	77	77	216
13	-31	25	259
14	88	87	28
15	37	42	138
16	123	109	119
17	-32	18	170
18	-36	39	193
H= 4		L= 4	
0	167	184	77
1	74	77	334
2	53	55	9
3	148	149	25
4	141	135	271
5	124	119	134
6	66	67	43
7	-29	20	195
8	65	67	304
9	57	55	306
10	104	106	247
11	58	58	207
12	85	83	111
13	74	67	11
14	38	30	230
15	43	48	21
16	-33	27	253
H= 4		L= 5	
0	64	66	266
1	-31	25	304
2	-30	11	323
3	55	53	160
4	74	65	339
5	102	103	118
6	43	43	157
7	36	45	38
8	60	61	187
9	-32	9	38
10	37	37	292
11	-34	21	114
12	-33	20	115
13	-35	12	349
H= 4		L= 6	
0	-31	17	328
1	-34	24	355
2	-35	36	357
3	-31	10	80
4	-34	29	345
5	38	38	136
6	-33	14	6
7	-32	13	347
8	-32	18	115
9	-34	22	19
H= 5		L= 0	
1	125	124	180
2	145	139	360
3	271	257	180
4	92	89	180
5	58	62	180
6	173	173	180
7	-28	16	180
8	188	199	360
9	102	107	180
10	-29	22	360
11	33	35	360
12	45	43	180
13	-29	9	360
14	-32	19	360
15	-31	19	360
16	-31	8	180
17	66	69	360
18	-32	4	0
H= 5		L= 1	
1	202	202	334
2	-28	29	311
3	47	47	26
4	58	61	199
5	89	89	177
6	-26	20	84
7	64	69	267
8	208	208	267
9	53	59	77
10	84	86	213
11	44	49	1
12	-34	28	153
13	-31	23	308
14	40	49	259
15	-35	24	58
16	-33	18	100
17	-34	29	307
18	-34	25	6
H= 5		L= 2	
1	107	107	352
2	83	83	93
3	57	56	210
4	53	60	333
5	85	87	178
6	74	78	39
7	123	128	107
8	89	88	283
9	-31	37	298
10	100	97	103
11	140	141	319
12	-32	22	123
13	57	59	343
14	-34	27	262
15	-35	30	260
16	-35	32	98
17	-34	18	268
H= 5		L= 3	
1	90	90	143
2	122	126	80
3	97	104	2
4	83	80	344
5	52	55	276
6	-29	26	231
7	84	79	270
8	104	102	191
9	122	118	72
10	47	47	236
11	-30	11	45
12	-30	8	220
13	49	57	180
14	38	40	134
15	58	54	88
16	-36	30	24
H= 5		L= 4	
1	34	33	279
2	57	56	153
3	109	107	76
4	60	62	217
5	43	42	266
6	121	115	32
7	-33	26	68
8	-32	15	19
9	71	69	77
10	-32	17	8
11	-31	4	285
12	-35	36	317
13	-32	0	97
H= 5		L= 5	
1	41	42	241
2	41	43	117
3	41	48	302
4	-32	19	329
5	-32	16	84
6	38	46	298
7	-34	30	187
8	43	42	28
9	-32	5	74
10	-36	34	54
H= 5		L= 6	
1	44	45	268
2	48	56	329
3	-34	23	172
4	-33	6	139
H= 6		L= 0	
0	-32	31	360
1	-28	19	360
2	65	69	180
3	32	36	180
4	63	61	180
5	81	82	180
6	65	65	180
7	68	67	180
8	-31	20	180
9	-32	32	180
10	35	41	360
11	36	46	180
12	-33	23	180
13	37	38	180
14	-35	35	360
15	-32	13	0
H= 6		L= 1	
0	136	138	42
1	90	83	78
2	-27	21	181
3	33	39	216
4	126	128	105
5	172	170	269
6	71	75	128
7	51	51	59
8	39	43	181
9	43	50	127
10	36	39	73
11	70	66	253
12	52	63	257
13	-31	11	303
14	-32	22	229
15	-32	16	351
H= 6		L= 2	
0	58	61	137
1	63	63	319
2	124	124	158
3	-31	31	17
4	45	48	7
5	48	54	132
6	173	168	325
7	-31	18	279
8	-33	32	239
9	44	53	159
10	36	49	137
11	102	101	135
12	-31	11	228
13	-32	23	18
14	-32	17	324
H= 6		L= 3	
0	60	59	56
1	100	103	280
2	49	50	199
3	107	108	220
4	66	67	302
5	56	66	129
6	62	67	355
7	54	51	41
8	37	32	308
9	-31	13	249
10	-34	28	288
11	-33	16	359
12	-33	22	186
13	-33	6	150
H= 6		L= 4	
0	37	44	299
1	45	51	190
2	-33	11	203
3	37	44	222
4	56	53	73
5	-32	14	114
6	-32	22	358
7	-32	12	5
8	-33	21	217
9	-33	18	304
10	-34	13	120
H= 6		L= 5	
0	-32	31	239
1	44	50	356
2	-35	28	96
3	-34	21	329
4	-34	1	94
5	-33	12	220
H= 7		L= 0	
1	160	159	360
2	140	131	180
3	-34	33	180
4	48	46	360
5	-30	5	0
6	71	65	180
7	-32	25	360
8	37	41	180
9	-31	1	360
10	-34	31	180
11	-32	16	360
12	40	47	360
H= 7		L= 1	
1	78	78	114
2	60	57	70
3	54	51	24
4	-31	24	32
5	-32	34	355
6	-32	18	39
7	-31	13	34
8	-31	12	63
9	-33	31	266
10	-34	31	182
11	48	51	176
H= 7		L= 2	
1	41	47	82
2	76	81	124
3	-31	6	229
4	49	54	299
5	-34	26	281
6	68	63	140
7	43	48	96
8	47	56	83
9	-32	8	117
10	-33	27	323
H= 7		L= 3	
1	89	79	328
2	47	50	69
3	-32	21	157
4	47	41	169
5	-33	26	122
6	-36	33	123
7	-32	15	196
8	40	36	24
H= 7		L= 4	
1	-36	32	305
2	56	58	25
H= 8		L= 0	
0	-32	24	180
1	-32	10	180
2	-34	20	360
3	-32	17	0
4	-36	37	0
5	40	45	360
H= 8		L= 1	
0	39	44	67
1	-32	17	193
2	44	48	266
3	-33	15	259
4	40	44	330

body, or when the internal vibrations are small enough to be neglected. This molecule does not meet these requirements. Likewise the assumption that all bonded atoms are vibrating in phase seems somewhat unlikely, especially for the atoms in the furazan rings. However, in the absence of facilities for a more detailed and rigorous treatment, a combination of these approximations was tried. Bond distance corrections were calculated for the carbon skeleton by the method of Cruickshank (1956b, 1961) and for the rest of the atoms assuming adjacent atoms vibrate in phase (Busing & Levy, 1964). Support for this assumption comes from the fact that the thermal vibration of all atoms increases perpendicular to the bonds as the distance from the center of the molecule increases. The corrected bond distances are given in Table 3, and a diagram of the molecule showing these distances is shown in Fig. 2.

Bond number calculations were made (Pauling, 1960) using the average corrected bond distances from Table 3. These calculations indicate bond numbers of 1·27 for the C–C, 1·46 for the type C(1)–N(1), 1·34 for the type C(2)–N(2), 1·74 for the type N(2)–O(2), 0·82 for the type N(2)–O(3), and 1·03 for the type N(3)–O(3) bonds.

Table 3. Interatomic distances in benzotrifuroxan

Atoms	Length (Å) Least-squares	Length (Å) Corrected for thermal motion
C(1)–C(2)	1·440 ± 0·007	1·454
C(2)–C(3)	1·401 ± 0·008	1·416
C(3)–C(4)	1·422 ± 0·007	1·435
C(4)–C(5)	1·425 ± 0·007	1·439
C(5)–C(6)	1·429 ± 0·008	1·444
C(6)–C(1)	1·407 ± 0·007	1·419
C(1)–N(1)	1·305 ± 0·007	1·316
C(3)–N(3)	1·322 ± 0·006	1·335
C(5)–N(5)	1·300 ± 0·007	1·316
C(2)–N(2)	1·318 ± 0·007	1·324
C(4)–N(4)	1·330 ± 0·007	1·336
C(6)–N(6)	1·336 ± 0·007	1·346
N(1)–O(1)	1·398 ± 0·005	1·403
N(3)–O(3)	1·380 ± 0·007	1·384
N(5)–O(5)	1·377 ± 0·005	1·380
N(2)–O(2)	1·211 ± 0·007	1·236
N(4)–O(4)	1·201 ± 0·006	1·225
N(6)–O(6)	1·207 ± 0·005	1·235
N(2)–O(3)	1·462 ± 0·006	1·469
N(4)–O(5)	1·475 ± 0·006	1·486
N(6)–O(1)	1·466 ± 0·007	1·473

Table 4. Distances of atoms from plane of molecule

Atom	Distance (Å)	Atom	Distance (Å)
C(1)	−0·036	N(4)	−0·042
C(2)	−0·016	N(5)	0·017
C(3)	0·021	N(6)	0·031
C(4)	0·010	O(1)	−0·033
C(5)	0·027	O(2)	−0·052
C(6)	0·013	O(3)	0·086
N(1)	−0·074	O(4)	−0·096
N(2)	−0·002	O(5)	−0·007
N(3)	0·085	O(6)	0·070

Table 5. Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the vibration ellipsoids

Atom	Axis i	B_i (Å²)	a (°)	b (°)	c (°)
C(1)	1	4·6 ± 0·3	38 ± 18	123 ± 8	72 ± 30
	2	3·0 ± 0·2	60 ± 8	33 ± 8	79 ± 11
	3	4·2 ± 0·3	111 ± 26	90 ± 19	21 ± 26
C(2)	1	3·2 ± 0·2	28 ± 39	107 ± 81	69 ± 23
	2	3·4 ± 0·2	77 ± 74	19 ± 73	76 ± 30
	3	5·1 ± 0·3	114 ± 7	98 ± 8	26 ± 7
C(3)	1	3·3 ± 0·2	3 ± 30	88 ± 371	93 ± 127
	2	3·3 ± 0·2	90 ± 392	19 ± 27	71 ± 22
	3	5·3 ± 0·3	87 ± 7	109 ± 7	19 ± 7
C(4)	1	4·8 ± 0·3	52 ± 8	124 ± 8	56 ± 8
	2	3·3 ± 0·3	77 ± 72	36 ± 35	57 ± 70
	3	3·2 ± 0·3	139 ± 33	102 ± 77	52 ± 66
C(5)	1	3·9 ± 0·3	36 ± 53	106 ± 16	58 ± 53
	2	3·1 ± 0·2	81 ± 14	17 ± 15	76 ± 14
	3	4·1 ± 0·3	124 ± 54	96 ± 20	35 ± 50
C(6)	1	3·3 ± 0·2	13 ± 34	79 ± 30	84 ± 18
	2	3·0 ± 0·2	103 ± 34	32 ± 14	61 ± 7
	3	5·1 ± 0·3	90 ± 8	119 ± 6	29 ± 6
N(1)	1	4·0 ± 0·3	36 ± 13	74 ± 9	122 ± 12
	2	5·4 ± 0·3	94 ± 15	23 ± 18	68 ± 20
	3	4·8 ± 0·3	54 ± 13	106 ± 22	40 ± 18
N(2)	1	4·0 ± 0·2	18 ± 39	74 ± 46	83 ± 12
	2	4·2 ± 0·3	105 ± 46	18 ± 43	100 ± 11
	3	5·6 ± 0·3	100 ± 8	83 ± 9	12 ± 9
N(3)	1	4·0 ± 0·3	24 ± 14	105 ± 13	109 ± 8
	2	4·7 ± 0·3	68 ± 15	32 ± 10	68 ± 8
	3	6·7 ± 0·4	80 ± 6	117 ± 7	29 ± 6
N(4)	1	5·5 ± 0·3	31 ± 9	114 ± 5	71 ± 11
	2	3·4 ± 0·2	71 ± 6	25 ± 6	74 ± 11
	3	4·4 ± 0·3	114 ± 12	97 ± 11	25 ± 12
N(5)	1	5·6 ± 0·3	33 ± 11	57 ± 10	85 ± 14
	2	4·1 ± 0·3	112 ± 10	47 ± 12	129 ± 16
	3	4·8 ± 0·3	113 ± 16	60 ± 16	40 ± 16
N(6)	1	3·8 ± 0·2	9 ± 13	92 ± 11	99 ± 11
	2	5·6 ± 0·3	94 ± 7	44 ± 11	134 ± 11
	3	4·6 ± 0·3	82 ± 14	46 ± 11	45 ± 12
O(1)	1	3·7 ± 0·2	29 ± 5	90 ± 4	119 ± 5
	2	6·2 ± 0·2	85 ± 7	9 ± 13	82 ± 12
	3	5·4 ± 0·2	61 ± 6	99 ± 13	30 ± 7
O(2)	1	5·6 ± 0·2	24 ± 6	71 ± 5	104 ± 4
	2	3·6 ± 0·2	114 ± 5	47 ± 3	127 ± 3
	3	8·6 ± 0·3	92 ± 4	50 ± 2	40 ± 2
O(3)	1	3·7 ± 0·2	25 ± 5	114 ± 5	86 ± 5
	2	5·3 ± 0·2	67 ± 6	26 ± 6	79 ± 10
	3	6·5 ± 0·3	98 ± 6	99 ± 10	12 ± 10
O(4)	1	8·0 ± 0·3	50 ± 3	124 ± 4	59 ± 3
	2	5·3 ± 0·2	62 ± 5	34 ± 4	73 ± 4
	3	3·3 ± 0·2	126 ± 3	87 ± 4	36 ± 3
O(5)	1	5·9 ± 0·2	20 ± 12	70 ± 11	86 ± 12
	2	5·1 ± 0·2	109 ± 13	39 ± 20	57 ± 22
	3	4·6 ± 0·2	83 ± 11	122 ± 20	33 ± 21
O(6)	1	3·4 ± 0·2	35 ± 2	125 ± 2	88 ± 3
	2	7·9 ± 0·3	66 ± 6	51 ± 8	48 ± 12
	3	7·0 ± 0·3	114 ± 6	122 ± 9	42 ± 12

These bond numbers indicate a substantial amount of resonance in the ring system. Weakening of the C–C bonds in the benzene ring by this resonance was found in benzotrifuroxan just as it was in 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965).

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The Structure of Fibrous Sulphur

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The structure of fibrous sulphur has been determined by a systematic use of the Fourier transform of its helical molecules. From this analysis, the helical molecules appeared to have two *incommensurable* repetition lengths in the direction of the helical axis, one being due to the succession of the atoms in that direction, the other to the pitch of the helix. A trial to substitute the two repetition lengths by a single one would result in an infinite repetition length. For this reason the structure is not crystallographic in the classical sense of the word, so we have chosen an improper 'unit cell' of orthorhombic symmetry, containing four helical molecules of supposedly infinite length, with the dimensions $a = 8\cdot11$ Å and $b = 9\cdot20$ Å, $c =$ indeterminate. The directions of a and b are normal to the helical axis, but only b is properly a repetition length.

In the direction of a the structure consists of alternating layers of right and left handed helices. Within each layer the helical molecules are screwed in or out, with respect to their neighbours, over half the atomic period along the molecule. This explains a peculiar extinction rule.

The molecular parameters, *i.e.* the bond distance, the bond angle and the dihedral angle, are compared with those of other sulphur molecules.

Introduction

Several physical properties of liquid sulphur suggest that above 160 °C it contains long chain molecules (see *e.g.* Schenk, 1956). One of the strongest arguments is provided by the X-ray fibre diagram, obtained from fibres made by highly stretching amorphous sulphur quenched from above 300 °C. This diffraction pattern was discovered by Trillat & Forestier (1932); after being wrongly interpreted initially by Meyer & Go (1934) as a one-component pattern, it was later proved (Prins, Schenk & Hospel, 1956) to be due to two components of which only one is soluble in carbon disulphide. The reflexions due to the soluble part were shown (Prins, Schenk & Wachters, 1957) to belong to a metastable ring modification S_γ (De Haan, 1958). The reflexions of the carbon-disulphide-insoluble part evidently formed a fibre diagram. The corresponding metastable modification was called S_ψ.

Schenk (1956), comparing S_ψ with hexagonal selenium, proposed a preliminary unit cell containing 10 atoms placed in three turns of a cylindrical-helical mol-