897. *Molecular Complexes. Part I. The Crystal and Molecular Structure of the* 1 : 1 *Adduct of Benzotrifuroxan and* 13,14-*Dithiatricyclo*[8,2,1,$1^{4,7}$]*tetradeca*-4,6,10,12-*tetraene*

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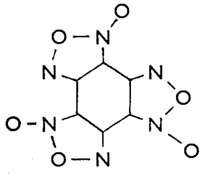
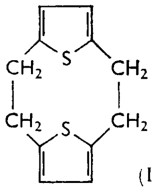
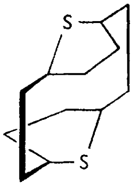
The structure of the 1 : 1 π-complex of the 13,14-dithiatricyclo[8,2,1,$1^{4,7}$]-tetradeca-4,6,10,12-tetraene (DTTD) and benzotrifuroxan has been determined by a three-dimensional method. The crystals are formed from plane-to-plane stacks in which pairs of thiophen donor groups of the DTTD molecules alternate with the electron-acceptor molecule, benzotrifuroxan. The DTTD has the *trans* or step-like form predicted from spectroscopic evidence, and in the benzotrifuroxan the furoxan systems have the expected furazan *N*-oxide form.

Hexanitrosobenzene or benzotrifuroxan (I) was first prepared by Turek[1] in 1931 but little was known about it until Bailey and Case[2] in 1958 showed that it formed, with aromatic hydrocarbons, a series of complexes of great stability. However, there was little or no physical or chemical evidence of its structure. At this time, Powell and Chantry[3] made a preliminary two-dimensional study of benzotrifuroxan, but abandoned it after having shown that the crystals were orthorhombic, $a = 6{\cdot}90$, $b = 19{\cdot}49$, and $c = 6{\cdot}49$ Å with the non-centrosymmetric space group $Pna2_1$.

Molecular complexes of benzotrifuroxan with an aromatic hydrocarbon system containing a heavy atom were then considered. In the preliminary work of Powell and Chantry,[3] when the heavy atoms were placed on the periphery of the hydrocarbon systems in α-bromonaphthalene and *p*-bromoaniline complexes, it was not possible to locate these atoms by two-dimensional methods. Powell and Prout[4] examined the structure of the complex of bis-8-hydroxyquinolinatocopper(II) and benzotrifuroxan but, unfortunately, after a detailed *X*-ray structure analysis, it appeared that the benzotrifuroxan was disordered. Several complexes with sulphur-containing aromatic compounds were prepared. The complexes with benzthiophen and 13,14-dithiatricyclo[8,2,1,$1^{4,7}$]tetradeca-4,6,10,12-tetraene (II) (DTTD) seemed the most suitable for structural work, though both crystals gave rather poor diffraction patterns. The latter was chosen because of the additional interest of the sulphur derivative.


(I)


(II)


(III)

If DTTD (II) has a centre of symmetry, as suggested by Winberg *et al.*[5] from a consideration of the lack of coincidences of the fundamentals of the Raman and infrared spectra and those of its oxygen analogue, then it must be either planar (D_{2h}) or have a *trans* or step-like structure (C_{2h}) (III). The step-like structure is the more probable, since it allows longer sulphur–sulphur contacts. With the benzotrifuroxan, it may lead to a

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[1] O. Turek, *Chimie et Industrie*, 1931, **26**, 785.
[2] A. S. Bailey and J. R. Case, *Tetrahedron*, 1958, **3**, 113.
[3] H. M. Powell and D. Chantry, personal communication.
[4] H. M. Powell and C. K. Prout, *J.*, 1965, 4882.
[5] H. E. Winberg, F. S. Fawcett, W. E. Madel, and C. W. Theobold, *J. Amer. Chem. Soc.*, 1960, **82**, 1428.

TABLE 1

Observed structure amplitudes and calculated structure factors for (*hkl*)

h	*k*	*l*	$5\|F_o\|$	$5F_c$
0	0	3	170	-164
		5	240	238
		6	35	-0
		7	94	-103
		8	104	85
		10	97	111
		12	78	-83
		13	51	-52
		14	37	-37
0	1	-12	92	80
		-10	75	58
		-9	59	42
		-7	130	108
		-6	52	-4
		-5	207	190
		-4	190	211
		-3	83	74
		-2	360	467
		1	333	-373
		2	78	77
		3	174	147
		4	75	90
		5	126	-118
		6	102	-92
		7	48	51
		9	45	-35
		10	183	-183
		11	67	-63
0	2	-11	114	114
		-10	43	47
		-9	142	-138
		-8	115	-114
		-7	138	117
		-6	148	118
		-5	21	-14
		-4	263	-324
		-3	30	37
		-2	216	-224
		-1	74	74
		0	110	-94
		1	231	-245
		3	107	-110
		4	95	-107
		6	54	-26
		7	82	85
		8	134	-123
		9	141	-148
		10	138	125
		11	80	105
0	3	-12	74	61
		-11	129	-131
		-10	112	-107
		-8	171	162
		-7	49	46
		-6	263	-282
		-5	216	-229
		-4	49	51
		-3	61	53
		-2	111	-104
		-1	136	-112
		1	144	157
		2	79	-71
		3	94	89
		4	29	14
		6	59	-66
		7	90	-88
		8	86	98
		9	156	159
0	4	-12	110	-94
		-11	74	55
		-10	62	42
		-9	60	-43
		-8	98	-77
		-7	52	-41
		-6	91	78
		-5	98	100
		-4	39	44
		-3	60	-55
		-2	119	-122
		-1	182	212
		0	99	96
		2	149	-158
		4	128	105
		5	48	54
		7	67	48
		8	51	-51
0	5	-11	72	63
		-7	67	-65
		-5	46	44
		-3	45	43
		-2	126	129
		0	64	-76
		1	62	-61
		2	86	98
		3	78	76
		4	37	-37
		5	114	-109
		7	62	67
0	6	-12	48	70
		-10	67	-65
		-9	51	-53
		-8	51	56
		-7	70	86
		-6	37	32
		-5	99	-101
		-4	36	34
		-3	36	36
		-2	62	-63
		-1	50	-50
		0	37	51
		2	33	23
		3	62	-75
1	-6	-4	46	-44
		-3	129	142
		-2	123	108
		-1	55	-53
		1	54	-31
		2	69	58
		3	108	104
		4	82	-86
		5	109	-110
		7	110	103
		8	82	79
		9	55	-57
		10	56	-58
1	-5	-5	62	50
		-4	53	55
		-3	79	-77
		-2	56	-43
		-1	74	-65
		0	86	104
		3	134	-155
		5	38	41
		7	123	-142
		8	64	-70
		10	53	31
1	-4	-7	59	-58
		-5	62	-55
		-2	46	-38
		-1	34	-55
		0	88	-83
		1	111	-127
		3	95	-94
		5	73	90
		6	92	-85
		8	131	144
		11	80	-76
		13	139	134
1	-3	-9	89	-93
		-8	112	-105
		-6	113	115
		-5	43	-42
		-4	128	-107
		-2	62	-51
		0	46	61
		1	111	117
		2	32	-58
		3	91	93
		4	84	67
		5	87	-94
		6	106	101
		7	95	93
		8	35	35
		9	91	-81
		11	127	124
		12	99	101
		13	87	-83
		14	77	-71
		16	56	67
1	-2	-11	54	-51
		-10	53	-51
		-9	44	51
		-8	170	177
		-7	50	52
		-6	115	-103
		-5	184	-181
		-4	157	156
		-3	270	258
		-1	28	-4
		0	153	-117
		1	239	330
		2	194	239
		3	65	-63
		4	50	17
		6	83	-73
		7	94	102

TABLE 1 (*Continued*)

h	k	l	$5\|F_o\|$	$5F_c$
		8	82	-67
1	-1	-15	42	-42
		-13	85	70
		-11	52	54
		-9	65	-55
		-7	109	101
		-5	156	152
		-4	32	-45
		-3	152	168
		-2	42	-17
		-1	106	86
		1	55	49
		2	222	-340
		3	43	-41
		4	54	59
		5	208	224
		6	47	-65
		8	91	-98
		9	82	110
		10	49	32
		12	102	-109
		14	71	55
1	0	-15	70	76
		-14	26	20
		-13	37	-41
		-12	119	-113
		-10	113	103
		-9	220	191
		-8	50	-39
		-7	199	-208
		-6	81	-69
		-5	32	37
		-4	157	-188
		-3	168	185
		-2	66	-79
		1	158	-186
		2	134	135
		3	88	-86
		4	39	44
		5	130	-110
		6	104	-92
		7	38	7
		8	79	92
		9	37	-13
		10	141	-143
		12	110	108
1	1	-12	59	68
		-11	52	49
		-10	39	-32
		-9	217	-248
		-8	34	-55
		-7	135	128
		-6	225	206
		-5	72	-59
		-3	174	213
		-2	293	-322
		-1	271	-302
		0	184	199
		1	195	-207
		2	136	133
		3	101	-142
		4	135	121
		5	84	-48
		6	79	16
		8	77	-80
		9	63	-80
		10	43	58
		11	62	77
1	2	-14	37	34
		-12	43	-56
		-11	92	-86
		-10	45	47
		-9	137	116
		-8	167	144
		-7	152	-147
		-6	237	-242
		-4	143	128
		-3	124	131
		-2	152	-154
		-1	220	-204
		0	117	-106
		1	227	247
		2	173	163
		3	216	-250
		4	95	-96
		5	56	-44
		6	82	47
		7	51	54
1	3	-12	51	39
		-10	58	66
		-9	69	-69
		-8	144	-136
		-7	29	32
		-6	149	139
		-5	91	-108
		-4	36	-40
		-3	158	-172
		-2	115	-95
		-1	287	285
		0	241	246
		1	147	-116
		2	236	-235
		4	193	197
		5	43	66
		6	35	-41
		7	46	-50
		8	57	56
		9	52	55
1	4	-18	29	-36
		-17	46	-69
		-15	52	51
		-12	45	-50
		-9	54	-45
		-8	43	-47
		-7	42	-27
		-6	80	69
		-5	91	83
		-4	89	96
		-3	74	60
		-2	65	47
		-1	68	-70
		0	151	-139
		1	61	42
		2	57	50
		3	133	121
		9	35	-50
		10	73	-89
1	5	-15	39	-44
		-14	35	-25
		-11	80	73
		-10	52	-57
		-9	45	-47
		-7	155	158
		-5	104	-85
		-4	95	-85
		-2	55	23
		-1	46	46
		1	66	63
		2	95	-79
1	6	-12	26	-25
		-11	37	-35
		-9	91	106
		-8	45	36
		-7	73	-68
		-6	83	-83
		-4	91	90
		-3	37	31
		-2	73	-83
		-1	45	-51
2	-7	1	42	33
		2	79	92
		3	29	-40
		4	73	-98
		6	42	40
		7	82	84
		8	29	-22
		9	42	-51
2	-6	-1	29	26
		2	137	-133
		3	76	-78
		4	61	75
		5	134	138
		7	100	-105
		8	78	-79
		9	82	88
2	-5	-5	39	35
		-4	34	-32
		-2	145	-138
		-1	36	-39
		0	25	20
		2	92	92
		3	36	38
		4	39	38
		5	104	-97
		6	111	-122
		8	75	64
		10	41	-39
		12	42	48
		13	42	62
2	-4	-10	42	45
		-9	93	-97
		-8	48	-44
		-7	90	58
		-6	93	101
		-5	31	-29
		-4	179	-202

TABLE 1 (*Continued*)

h	k	l	$5\lvert F_o\rvert$	$5F_c$
		-3	100	-83
		-2	196	241
		-1	145	160
		0	123	-128
		1	149	-157
		2	34	-20
		3	19	-32
		4	101	95
		5	67	69
		6	37	-22
		7	46	-65
		8	96	88
		10	60	50
		11	39	50
		12	42	-54
		13	29	-31
		15	39	51
		16	45	53
2	-3	-11	42	-45
		-9	75	82
		-8	57	42
		-7	56	-71
		-6	72	-56
		-5	196	-197
		-4	226	256
		-3	198	249
		-2	109	-100
		-1	110	-104
		0	111	-103
		1	249	285
		2	199	180
		3	61	-50
		4	88	-83
		5	83	-87
		6	176	151
		7	143	142
		9	61	-58
		10	37	-34
		11	48	-44
		12	41	48
2	-2	-13	51	56
		-8	25	62
		-6	190	186
		-5	78	-4
		-4	73	67
		-3	117	-117
		-2	149	142
		-1	120	-125
		0	17	19
		1	128	157
		2	54	22
		4	117	116
		5	84	58
		6	131	-140
		7	258	-274
		10	45	47
		11	48	-51
		12	41	-42
2	-1	-14	75	72
		-12	64	-85
		-10	114	112
		-9	25	45
		-8	104	-109
		-7	29	-7
		-6	45	30
		-5	72	-94
		-4	137	169
		-3	119	-131
		-2	211	284
		2	268	-290
		3	57	-47
		4	93	-78
		5	245	-285
		7	189	221
		8	59	29
		9	52	-30
		10	210	-192
		12	78	66
		13	42	56
2	0	-16	42	38
		-14	65	-71
		-12	72	66
		-11	119	119
		-10	148	-148
		-9	74	-50
		-7	167	145
		-6	53	57
		-5	192	-181
		-4	307	-334
		-3	107	100
		-2	361	-326
		0	58	22
		1	75	67
		4	67	-55
		5	130	138
		6	36	-74
		7	51	-44
		8	48	-51
		9	51	46
		10	88	94
		11	92	91
2	1	-12	49	-36
		-11	104	-95
		-10	43	-31
		-9	97	101
		-7	86	-79
		-6	123	-110
		-4	153	140
		-3	181	176
		-2	97	-78
		-1	97	-102
		0	96	97
		1	236	228
		2	74	57
		3	164	-138
		4	98	-74
		5	70	86
		6	183	195
2	2	-16	61	-83
		-15	61	-62
		-14	73	87
		-13	66	62
		-12	29	-37
		-11	47	-41
		-10	45	62
		-9	51	40
		-7	68	-55
		-6	128	113
		-5	68	65
		-3	57	76
		-2	30	52
		-1	160	158
		0	74	-58
		1	55	-54
		2	91	-77
		4	189	183
		6	126	-110
2	3	-15	82	102
		-13	73	-79
		-10	96	99
		-7	72	65
		-6	23	29
		-5	57	-63
		-1	96	-86
		0	39	-35
		1	33	32
		2	69	80
		4	57	-48
		5	39	-54
		8	42	56
		9	51	-65
2	4	-15	27	-33
		-13	42	47
		-12	63	42
		-10	65	-62
		-9	121	-106
		-8	27	26
		-7	90	100
		-5	131	-141
		-4	25	37
		-2	58	59
		-1	66	-84
2	5	-12	50	-48
		-7	125	-145
		-6	72	-72
		-5	117	119
		-4	59	61
		-3	51	-37
		0	79	83
		1	73	87
		2	66	-62
		5	43	46
2	6	-9	29	-35
		-8	41	-45
		-7	72	90
		-6	66	61
		-4	51	-39
		-1	41	28
3	-7	-1	48	-30
		0	48	-52
		1	34	36
		3	93	-96
		4	58	63
		5	82	89
		7	106	-95
		8	75	-68

TABLE 1 (*Continued*)

h	k	l	$5\|F_o\|$	$5F_c$
		9	38	60
		10	46	47
3	-6	-7	91	-85
		-5	48	60
		-4	34	43
		-3	64	-49
		-2	89	-79
		0	98	85
		3	68	57
		5	98	-96
		7	89	75
		8	57	59
		9	48	23
		10	48	-28
3	-5	-7	34	56
		-6	63	48
		-4	149	-145
		-2	154	140
		-1	152	141
		0	102	-91
		1	38	-36
		3	91	77
		7	65	-46
		8	44	35
		9	57	54
		10	93	-79
3	-4	-11	82	83
		-10	48	56
		-9	47	-54
		-8	46	-55
		-5	48	36
		-4	60	50
		-3	151	133
		-2	46	-47
		-1	122	-114
		0	92	-88
		1	141	137
		2	75	67
		3	188	-193
		4	142	-141
		5	101	96
		6	126	127
		8	131	-119
		9	115	-96
		10	87	75
		12	48	-46
3	-3	-13	57	67
		-12	74	60
		-11	103	-98
		-10	81	-82
		-9	69	63
		-4	48	-9
		-3	154	-146
		-2	65	15
		-1	128	121
		0	23	-32
		1	60	-51
		2	188	-232
		3	71	56
		4	99	118
		5	116	120
		6	149	-160
		7	172	-164
		8	94	93
		9	101	86
3	-2	-13	68	-66
		-12	117	-119
		-10	83	70
		-9	65	61
		-8	75	-65
		-6	46	61
		-4	48	48
		-3	247	-266
		-2	91	-92
		-1	46	37
		0	185	239
		1	85	79
		2	52	53
		3	109	104
		4	40	-48
		5	99	-83
		7	86	78
		9	64	-43
		12	83	69
3	-1	-12	128	136
		-11	58	33
		-9	118	-107
		-7	140	135
		-5	163	-179
		-4	128	-136
		-3	73	62
		1	182	-254
		2	60	82
		3	104	91
		6	74	53
		11	67	-33
3	0	-16	44	45
		-14	69	59
		-11	44	-40
		-9	102	104
		-8	54	-11
		-7	32	27
		-5	26	35
		-4	110	122
		-3	66	-73
		-2	28	-355
		-1	259	-315
		0	176	171
		1	195	204
		3	93	-96
		4	103	-85
		5	87	65
		8	63	-81
		11	59	38
3	1	-11	78	-75
		-10	63	-54
		-9	62	54
		-6	138	-141
		-4	101	-100
		-3	42	61
		0	42	18
		1	76	-79
		2	62	-60
		3	87	86
		4	81	67
		5	62	54
		6	103	-92
		7	77	-76
		9	82	98
		11	34	-43
3	2	-14	49	34
		-13	85	-84
		-12	76	-64
		-11	69	56
		-10	110	106
		-8	141	-149
		-7	119	-99
		-6	108	106
		-5	94	95
		-4	53	-31
		-3	46	35
		-2	41	59
		-1	78	72
		0	80	-78
		1	92	83
		2	86	71
		4	93	-90
		5	70	-55
		6	80	81
		7	122	129
		9	83	-82
		10	33	-26
3	3	-14	68	-59
		-13	69	70
		-12	69	57
		-11	47	-42
		-10	74	-60
		-8	109	111
		-7	127	116
		-5	91	-79
		-4	70	-68
		-3	125	121
		-2	28	30
		-1	29	-28
		0	107	-103
		1	30	50
		2	63	43
		6	48	-47
		7	34	-31
3	4	-7	33	-42
		-5	45	48
		-4	90	88
		-2	91	-93
		-1	46	-46
		0	74	86
		1	29	23
		2	48	-50
		3	109	-94
		5	69	68
3	5	-14	40	50
		-12	54	-49
		-10	46	47
		-7	34	-47
		-4	77	-68
		-3	34	-42
		-2	59	71

TABLE 1 (*Continued*)

h	k	l	$5\|F_o\|$	$5F_o$
		1	64	-70
		3	50	72
4	-7	1	46	51
		2	33	-37
		3	65	-65
		5	65	56
		6	33	32
		8	34	-32
4	-6	-5	58	-86
		-4	74	-70
		-2	117	123
		1	106	-81
		5	69	-49
4	-5	-4	73	54
		-2	96	-95
		-1	87	-73
		0	26	61
		2	36	17
		3	45	45
		6	109	104
		8	76	-73
		9	45	-35
		11	82	81
4	-4	-9	46	36
		-8	100	100
		-6	29	-46
		-5	54	52
		-4	71	-44
		-1	119	102
		3	62	-59
		4	65	58
		5	59	65
		7	107	-104
		9	85	85
		10	56	57
		1	82	-87
		12	75	-67
4	-3	-10	144	142
		-8	124	-118
		-7	76	-80
		-6	99	92
		-5	131	127
		-4	36	-49
		-3	63	-53
		-2	69	-55
		-1	124	120
		0	43	53
		1	60	-62
		2	53	-65
		4	94	-99
		7	37	38
4	-2	-11	46	-44
		-10	61	-60
		-9	29	28
		-8	44	38
		-7	43	68
		-6	31	-52
		-4	87	-107
		-3	63	57
		0	148	-240
		1	36	-46
		2	81	84
h	k	l	$5\|F_o\|$	$5F_c$
		3		104
		5	68	40
		6	54	-63
		7	46	62
		12	58	57
4	-1	-14	46	-39
		-12	33	39
		-11	70	67
		-10	30	-20
		-9	134	-114
		-8	36	-44
		-6	103	-94
		-5	121	121
		-3	59	-64
		-2	38	6
		-1	20	-128
		8	67	-77
		10	66	81
4	0	-11	132	-133
		-9	117	107
		-8	120	97
		-7	46	-32
		-5	57	79
		-4	156	-150
		-3	155	-142
		-2	196	219
		8	45	59
		9	65	58
		10	58	-45
		11	54	-55
4	1	-13	55	-57
		-12	38	40
		-11	92	96
		-10	79	77
		-9	118	-100
		-8	155	-148
		-7	30	31
		-6	138	125
		-5	59	51
		-4	100	-93
		-3	55	-53
		-2	35	-40
		-1	111	107
		0	102	78
		1	136	-139
		5	38	30
		9	39	-39
4	2	-14	27	29
		-13	47	52
		-12	47	42
		-11	74	-56
		-10	111	-107
		-8	135	130
		-6	71	-70
		-5	97	-105
		-3	196	180
		-2	135	121
		-1	148	-120
		0	158	-158
		1	51	32
		2	137	125
		4	38	-34
h	k	l	$5\|F_o\|$	$5F_c$
		5	38	-32
		6	38	36
4	3	-6	56	54
		-5	50	42
		-3	88	-83
		-2	142	-112
		-1	70	62
		0	72	69
		1	101	79
		2	58	-61
		3	54	-47
		9	22	21
4	4	-9	61	61
		-7	55	-52
		-6	47	-43
		-2	33	26
		-1	39	29
		0	101	-81
		1	47	-47
		-3	27	39
4	5	-11	42	64
		-9	51	-66
		-8	46	-44
		-6	54	57
		-4	33	-52
		-3	38	-30
4	6	-10	33	-33
		-9	30	31
		-8	31	51
		-5	23	-23
		0	20	-20
5	-6	0	41	60
		1	34	34
		3	66	-79
		4	53	-60
		6	70	72
		8	45	-58
5	-5	-6	56	-68
		-4	90	107
		-3	62	72
		-2	67	-63
		-1	65	-66
		2	45	47
		3	41	25
		8	43	50
		9	26	33
		10	37	-45
5	-4	-9	58	-61
		-8	56	-43
		-7	59	-63
		-6	137	139
		-5	118	107
		-4	86	-72
		-3	83	-80
		-1	116	121
		0	89	67
		1	68	-59
		2	60	-63
		3	34	-39
		4	45	53
		5	39	44
		7	39	-32

TABLE 1 (*Continued*)

h	k	l	$5\|F_o\|$	$5F_c$
		8	24	−33
		9	36	−35
5	−3	−12	53	23
		−10	26	−5
		−8	82	90
		−7	48	−26
		−6	20	−42
		−5	128	−97
		−4	33	42
		−2	14	20
		−1	29	18
		0	64	−80
		1	27	5
		2	37	68
		3	14	−15
		4	71	−76
		5	107	−102
		6	29	20
		7	38	48
		9	24	−36
5	−2	−10	78	−68
		−7	70	−59
		−6	106	73
		−4	79	74
		−3	56	−52
		−2	175	−256
		2	20	−32
		3	66	−84
		4	31	20
		5	143	162
		6	30	14
		7	56	−51
		8	108	−105
		10	74	68
		11	37	43
5	−1	−12	93	−104
		−11	68	−60
		−10	34	32
		−9	90	88
		−7	103	−89
		−6	122	−121
		−5	87	74
		−4	109	−99
		−3	18	6
		−2	79	115
		−1	89	89
		1	24	25
		2	20	−27
		3	95	85
		4	16	−10
		5	51	−44
		6	28	−31
		7	48	44
		8	81	78
		9	65	61
		10	41	−41
		11	45	−54
5	0	−13	53	−64
		−11	95	108
		−9	72	−77
		−8	68	−77
		−7	56	52
		−6	131	127
		−5	77	74
		−2	60	48
		−1	96	98
		1	97	−83
		3	49	36
		4	94	88
		8	53	−54
5	1	−16	49	51
		−15	38	36
		−14	24	−15
		−12	41	38
		−10	31	−35
		−8	115	104
		−7	54	37
		−6	59	−41
		−3	86	73
		−2	46	−36
		−1	107	−99
		0	64	−48
		2	111	105
		4	96	−92
5	2	−17	45	65
		−15	36	−52
		−12	41	39
		−8	43	−32
		−7	60	−52
		−3	94	−81
		−2	58	−39
		−1	52	43
		0	68	75
		2	63	−69
		3	46	−39
5	3	−12	40	−48
		−11	41	−43
		−10	34	22
		−9	41	54
		−7	92	−78
		2	41	32
5	4	−14	36	−37
		−11	44	60
		−10	39	−37
		−9	80	−97
		−8	33	−30
		−7	92	99
		−6	34	46
		−5	34	−33
5	5	−8	50	49
		−7	41	−28
		−6	41	−51
		−3	29	25
		−2	28	−36
6	−8	−2	16	−19
		1	33	−49
6	−7	−4	17	−31
		−3	30	16
		−2	58	46
		1	51	52
6	−6	6	34	−22
		5	26	−45
		−4	74	87
		−3	63	62
		−2	71	−58
		−1	28	−24
		0	22	−20
6	−5	−6	33	38
		−5	56	58
		−4	82	−71
		−3	96	−87
		−2	26	−17
		−1	87	87
		0	39	41
		1	135	−109
		2	80	−74
6	−4	−6	67	−55
		−5	117	−93
		−3	85	73
		−1	82	−81
		0	122	−121
		1	66	78
		5	74	−78
		6	75	70
		7	73	67
6	−3	−10	46	−43
		−9	30	−13
		−7	52	−25
		−5	71	−66
		−3	43	13
		−2	59	59
		−1	42	42
		0	49	51
		1	21	24
		3	45	−59
		4	28	28
		5	79	84
		6	36	13
		7	60	−49
		10	46	50
6	−2	−16	14	−15
		−15	12	41
		−14	69	69
		−12	36	−58
		−11	71	−77
		−10	27	20
		−9	74	87
		−7	57	−73
		−6	22	−37
		−5	81	61
		−4	246	318
		−3	78	−84
		0	58	57
		1	59	57
		5	34	−37
		8	19	13
		10	33	−39
6	−1	−14	19	−35
		−13	24	−38
		−12	20	27
		−11	82	92
		−10	19	−9
		−9	34	−27
		−8	38	−17
		−7	40	41
		−6	83	69

TABLE 1 (*Continued*)

h	*k*	*l*	5|*F*o|	5*F*c
		−5	41	−46
		−4	124	−127
		−3	55	−67
		−2	85	92
		−1	102	118
		0	36	−22
		1	65	−73
		2	32	−33
		3	32	31
		6	19	−25
6	0	−10	12	3
		−9	12	17
		−8	23	−14
		−6	48	−54
		−5	25	41
		−3	53	35
		−1	83	−85
		0	28	−31
		2	35	42
		4	61	−64
		5	33	−29
		6	52	63
		7	19	42
		8	19	−35
		9	19	−21
6	1	−15	29	−39
		−14	19	−26
		−13	26	29
		−12	33	40
		−10	38	−51
		−9	26	−23
		−8	25	38
		−7	24	39
		−6	24	−10
		−3	39	−20
		−2	56	−55
		−1	57	60
		0	41	52
		1	31	−19
		2	62	−72
		3	34	−26
		4	57	59
		5	60	65
		6	34	−54
		7	41	−53
		9	39	35
6	2	−16	14	−19
		−14	24	28
		−13	25	−38
		−12	34	−46
		−10	34	65
		−9	34	39
		−8	34	−38
		−7	55	−68
		−5	38	55
		3	19	20
		7	22	24
		8	21	30
6	3	−12	19	35
		−10	19	−27
		−9	33	−52
		−7	38	59
		−6	33	47
		−5	19	−34
		−4	38	−49
		−2	38	56
		1	26	−33
		3	35	36

plane-to-plane stacked, " charge transfer " or polarisation-bonded complex with two donor groups alternating with one acceptor, the benzotrifuroxan.

The compound forms bright yellow needle-like crystals stable in the *X*-ray beam and in the atmosphere.

Crystal Data.—$H_{12}C_{18}N_6O_6S_2$, $M = 472{\cdot}5$, triclinic pinacoidal, $a = 9{\cdot}71 \pm 0{\cdot}03$, $b = 8{\cdot}01 \pm 0{\cdot}03$, $c = 15{\cdot}28 \pm 0{\cdot}03$ Å, $\alpha = 102{\cdot}2 \pm 0{\cdot}2$, $\beta = 96{\cdot}2 \pm 0{\cdot}2$, $\gamma = 117{\cdot}9 \pm 0{\cdot}2°$; $U = 996{\cdot}7$ Å^3, $D_m = 1{\cdot}566$, $Z = 2$; $D_c = 1{\cdot}574$, $F(000) = 484$; space group $P\bar{1}$ (C_i^1, No. 2); Cu-K_α radiation, $\mu = 28{\cdot}1$ cm.$^{-1}$; single crystal oscillation and Weissenberg photographs. Optically biaxial.

A three-dimension Patterson function sharpened to " point atoms at rest " was computed from 1192 independent reflections. By assuming the centric space group, it was possible to assign the most prominent features to sulphur–sulphur vectors and to locate the two sulphur atoms.

A three-dimensional electron-density distribution from the phases given by the positions of the sulphur atom was then computed by the use of Rollett's[6] FATAL (Fourier analysis testing for atomic locations) programme. Of fifty-nine maxima over about 4 eÅ^{-3} located by the programme, twenty-six could be interpreted as light-atom positions. A second cycle, in which phases from the positions of the sulphur atoms and these light atoms were used, revealed all the thirty light-atom positions, and showed one only of the first twenty-six to be in error. Positional parameters and isotropic temperature factors were then improved by use of an F_o–F_c synthesis, the resulting model giving a reliability index of 0·29. The structure was then refined by the least-squares method on the assumption of anisotropic thermal motion, and by using a block diagonal approximation to the normal matrix. In all, nine refinement cycles were computed. For the first four cycles, weights were assumed for all terms, then followed a detailed examination of the intensity values with the correction of several errors. Next, three refinement cycles were computed by using the weighting scheme

$$\sqrt{\omega} = \sqrt{\frac{1}{1 + \left(\frac{|F_o| - b}{a}\right)^2}}$$

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[6] J. S. Rollett, personal communication.

TABLE 2

Atomic co-ordinates (× 10^4) and standard deviations (× 10^4)

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
S(1)	2760	6	2827	6	2236	3
S(2)	6223	6	5155	6	1850	3
C(1)	3842	23	5335	24	2911	10
C(2)	2551	25	3402	23	1224	10
C(3)	3749	26	6415	25	2331	13
C(4)	3043	27	5338	28	1404	13
C(5)	6437	26	4665	25	2942	11
C(6)	5089	27	2630	23	1150	14
C(7)	5948	31	2638	33	2684	16
C(8)	5161	30	1557	28	1771	15
C(9)	4780	31	5773	30	3779	15
C(10)	6514	38	5999	30	3724	13
C(11)	2429	33	1950	35	310	16
C(12)	4081	34	2141	27	210	12
C(13)	9908	33	3536	29	3342	15
C(14)	1018	29	5540	31	3863	10
C(15)	1138	24	6973	23	3437	14
C(16)	456	25	6347	24	2411	12
C(17)	9476	25	4330	24	1927	10
C(18)	9331	26	2978	22	2473	12
N(1)	9682	25	1864	29	3621	12
N(2)	1946	27	6428	28	4815	14
N(3)	2171	30	8872	32	4057	16
N(4)	502	26	7538	28	1940	12
N(5)	9016	20	4217	26	1107	10
N(6)	8356	23	795	28	2015	13
O(1)	10,149	23	1645	24	4370	11
O(2)	2644	18	8376	18	4918	9
O(3)	2804	27	449	23	4018	14
O(4)	9723	21	6283	18	1063	10
O(5)	8193	21	2884	23	381	11
O(6)	8645	20	152	19	2751	10

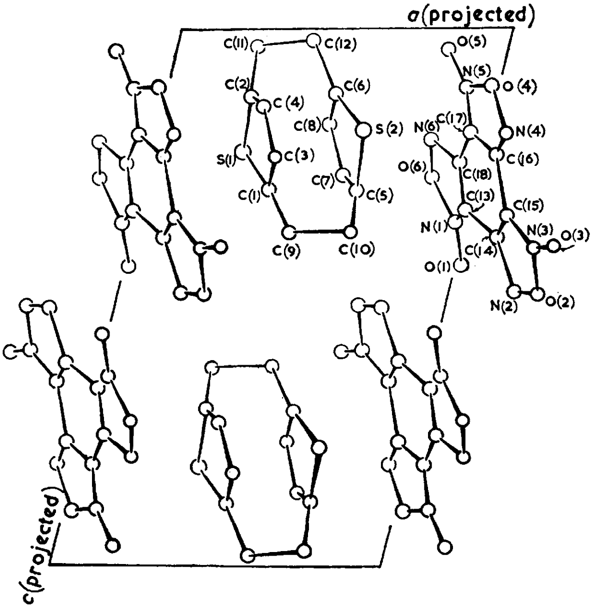


FIGURE 1. The molecular arrangement in the crystal projected down the *b* axis

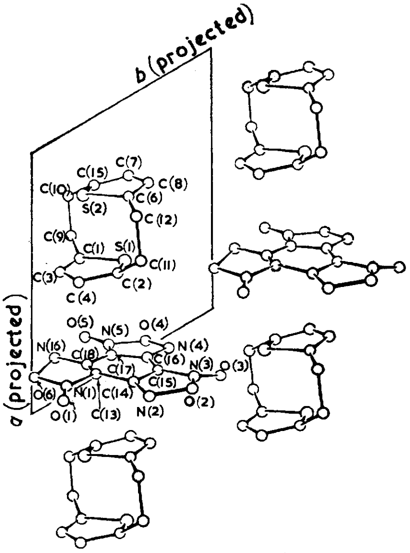


FIGURE 2. Part of two of the plane-to-plane stacks in the crystal, projected down the *c* axis. The step-like form of the 13,14-dithiatricyclo$[8,2,1,1^{4,7}]$tetradecan-4,6,10,12-tetraene is clearly visible

TABLE 3

Thermal parameters (× 10^4): the temperature factor, T, is equal to
$2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)}$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{23}
S(1)	274	177	63	61	86	92
S(2)	208	195	46	30	78	160
C(1)	329	318	26	18	28	265
C(2)	442	265	24	−2	90	188
C(3)	446	363	99	200	279	676
C(4)	437	478	92	235	201	626
C(5)	429	343	46	37	104	380
C(6)	436	97	123	0	69	160
C(7)	542	656	147	255	293	1011
C(8)	513	404	113	261	100	394
C(9)	595	483	123	187	320	854
C(10)	968	465	47	119	−59	689
C(11)	561	617	115	224	109	485
C(12)	795	304	43	−27	77	325
C(13)	715	418	122	275	392	646
C(14)	518	707	2	−4	−74	672
C(15)	273	120	121	−187	−146	26
C(16)	466	285	77	226	142	491
C(17)	425	354	20	103	22	14
C(18)	441	140	75	72	29	100
N(1)	467	792	116	370	88	504
N(2)	479	582	149	156	155	230
N(3)	754	869	205	575	593	1029
N(4)	567	583	85	−24	74	437
N(5)	251	671	55	−105	60	179
N(6)	430	837	133	333	287	908
O(1)	649	735	131	211	238	698
O(2)	371	277	121	−163	22	26
O(3)	901	544	258	410	654	923
O(4)	632	344	129	224	271	329
O(5)	481	657	143	260	142	231
O(6)	595	348	125	140	230	381

TABLE 4

Atomic co-ordinates (Å) referred to the orthogonal axes a, b', and c^*

	X'	Y'	Z'		X'	Y'	Z'
S(1)	1·259	−0·998	−3·246	C(15)	−2·069	−3·382	−4·990
S(2)	3·806	−2·827	−2·686	C(16)	−2·332	−3·401	−3·499
C(1)	1·258	−2·470	−4·225	C(17)	7·264	−2·218	−2·796
C(2)	1·001	−1·860	−1·776	C(18)	7·546	−1·016	−3·588
C(3)	0·853	−3·494	−3·382	N(1)	8·123	0·288	−5·255
C(4)	0·721	−3·148	−2·038	N(2)	−1·298	−2·378	−6·989
C(5)	4·025	−1·989	−4·269	N(3)	−1·879	−4·449	−5·887
C(6)	3·768	−1·355	−1·669	N(4)	−2·661	−4·455	−2·815
C(7)	4·354	−0·672	−3·895	N(5)	6·990	−2·506	−1·606
C(8)	4·143	−0·317	−2·569	N(6)	7·494	0·323	−2·294
C(9)	1·865	−2·390	−5·485	O(1)	8·541	0·779	−6·342
C(10)	3·472	−2·580	−5·404	O(2)	−1·370	−3·711	−7·138
C(11)	1·578	−1·245	−0·450	O(3)	1·915	1·486	−5·831
C(12)	3·122	−1·427	−0·313	O(4)	6·904	−3·990	−1·542
C(13)	7·757	−1·020	−4·850	O(5)	6·808	−1·889	−0·553
C(14)	−1·413	−2·178	−5·606	O(6)	7·900	1·109	−3·993

where $a = 34$ and $b = 101$, the scale being that of Table 1. At this stage, hydrogen atoms at positions estimated with the aid of an F_o–F_c map were added and a final two cycles of refinement were then computed without further change of weighting scheme. The final reliability index for observed reflections was 0·137. Table 1 lists the observed structure amplitudes and calculated structure factors based on the final atomic co-ordinates given in Table 2. The standard deviations are minimum values deduced from the block diagonal approximation to the normal matrix. The thermal parameters are given in Table 3.

The atomic co-ordinates (in Å) in Table 4 are referred to the orthogonal axes, *a*, *b*′, and *c** where *c** is the reciprocal *C* axis and *b*′ lies on the same side of the *ac** plane as *b*. Some interatomic distances, together with standard deviations deduced from the formulæ of Cruickshank and Ahmed[7] are listed in Table 5. The inter-bond angles are given in Figure 5. The standard deviation in angles according to the formula of Darlow[8] vary between 1 and 3°.

TABLE 5

Some interatomic distances (Å) and angles (standard deviations in parentheses)

(*a*) *Within the* 13,14-*dithiatricyclo*[8,2,1,$1^{4,7}$] *tetradeca*-4,6,10,12-*tetraene*

S(1)–S(2)	3·19(0·01)	C(6)–C(8)	1·38(0·03)
S(1)–C(1)	1·77(0·03)	C(6)–C(12)	1·53(0·04)
S(1)–C(2)	1·71(0·02)	C(7)–C(8)	1·42(0·05)
S(2)–C(5)	1·78(0·02)	C(9)–C(10)	1·67(0·05)
S(2)–C(6)	1·78(0·03)	C(11)–C(12)	1·55(0·05)
C(1)–C(3)	1·39(0·03)	C(1)–C(5)	2·82(0·03)
C(1)–C(9)	1·38(0·04)	C(2)–C(6)	2·80(0·04)
C(2)–C(4)	1·35(0·04)	S(1)–C(6)	3·00(0·03)
C(2)–C(11)	1·56(0·04)	S(1)–C(5)	3·12(0·03)
C(3)–C(4)	1·40(0·04)	S(2)–C(1)	3·02(0·02)
C(5)–C(7)	1·49(0·05)	S(2)–C(2)	3·07(0·03)
C(5)–C(10)	1·38(0·04)		

(*b*) *Within the benzotrifuroxan molecule*

C(13)–C(14)	1·45(0·06)	C(18)–N(6)	1·52(0·05)
C(13)–C(18)	1·26(0·04)	N(1)–O(1)	1·29(0·03)
C(13)–N(1)	1·42(0·03)	N(1)–O(6)	1·52(0·04)
C(14)–C(15)	1·35(0·03)	N(2)–O(2)	1·33(0·04)
C(14)–N(2)	1·48(0·04)	N(3)–O(2)	1·56(0·03)
C(15)–C(16)	1·56(0·04)	N(3)–O(3)	1·11(0·05)
C(15)–N(3)	1·43(0·05)	N(4)–O(4)	1·34(0·04)
C(16)–C(17)	1·39(0·05)	N(5)–O(4)	1·47(0·03)
C(16)–N(4)	1·30(0·03)	N(5)–O(5)	1·22(0·04)
C(17)–C(18)	1·48(0·03)	N(6)–O(6)	1·37(0·03)
C(17)–N(5)	1·26(0·03)		

(*c*) *Between benzotrifuroxan and* 13,14-*dithiatricyclo*[8·2,1,$1^{4,7}$] *tetradeca*-4,6,10,12-*tetraene*

S(1)–C(18)	3·46	C(4)–C(16)	3·39
S(2)–O(6)	3·41	C(6)–O(5)	3·41
C(1)–C(14)	3·26	C(7)–C(18)	3·17
C(3)–C(15)	3·31	C(8)–N(6)	3·41
C(3)–C(16)	3·20		

The crystals are made up of isolated molecules of DTTD and benzotrifuroxan (I), stacked plane-to-plane with their planes approximately parallel to the (101) plane of the crystal (Figures 1 and 2).

The DTTD molecule has the step-like (C_{2h}) configuration suggested by Winberg *et al.*[4] The molecule is only approximately centrosymmetric. It is essentially similar to di-*m*-xylylene or di-*p*-xylylene.

All the bonded contacts have the expected lengths within the experimental error of the determination, but the planar systems are considerably distorted. Each thiophen ring is boat-shaped, and the carbon atoms bonded to the ethylene bridges are about 0·08—0·10 Å from the plane of the remaining three atoms of each ring. The least-squares best planes through each thiophen ring are almost exactly parallel (Figure 3). The contact distances of 2·80 and 2·82 Å between pairs of carbon atoms attached to the ethylene bridges are the same as those observed in di-*p*-xylylene. The sulphur–sulphur contact of 3·19 Å is about 1 Å longer than that predicted for an unstrained model, but still about 0·5 Å shorter than the expected Van der Waals contact distance. The sulphur atoms also make two short contacts of 2·99 [S(1)–C(6)] and 3·02 Å [S(2)–C(1)] with carbon atoms both considerably shorter than the sum of Van der Waals radii.

[7] D. W. J. Cruickshank and F. R. Ahmed, *Acta Cryst.*, 1953, **6**, 385.

[8] S. F. Darlow, *Acta Cryst.*, 1960, **13**, 683.

In general, the interatomic distances in the benzotrifuroxan molecule are in rather poor agreement with expected values. In particular, one of the furoxan rings is rather different from the other two, and there is considerable variation in length of the carbon bonds in the benzene nucleus. It is perhaps noteworthy that Britton and Noland [9] found unexpected ring-carbon distances in a chlorobenzofuroxan. Certain general tendencies can be seen: first, in general, the carbon–carbon bonds within the furoxan rings are rather shorter than those outside the rings. The ring oxygen atom is not equidistant from the two nitrogens, to which it is linked, but is closer to that not attached to the peripheral oxygen atom. The two nitrogen–carbon bonds are not equal in length. The bond between the carbon atom and the nitrogen atom bound to two oxygens is somewhat shorter. The most probable dimensions of the furoxan system, based on this work and that of Britton and Noland,[8] are given in Figure 4. The carbon–nitrogen bonds are therefore essentially single bonds (cf. Ph·NO_2 1·48 and Ph·$NHCOCH_3$ 1·43 Å). The nitrogen–

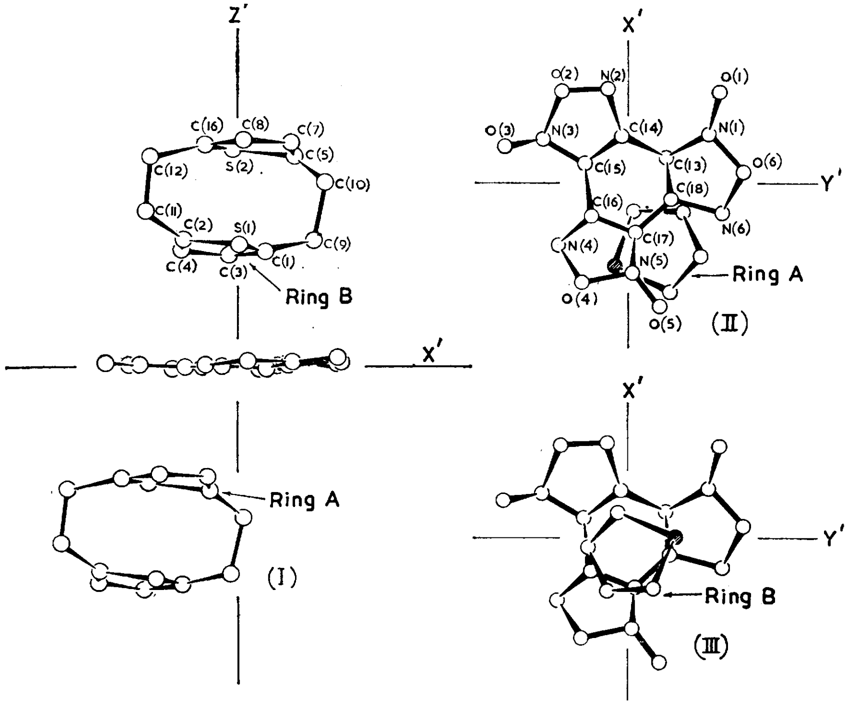
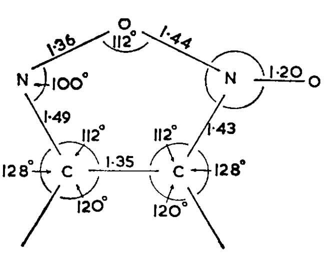


FIGURE 3. In (I) two 13,14-dithiatricyclo[8,2,1,$1^{4,7}$]tetradeca-4,6,10,12-tetraene molecules are projected perpendicular to the least-squares best plane of the benzene nucleus of the benzotrifuroxan molecule. The relationships between the two thiophen rings, A and B, of the 13,14-dithiatricyclo[8,2,1,$1^{4,7}$]tetradeca-4,6,10,12-tetraene molecules and the benzotrifuroxan are shown in (II) and (III), respectively

FIGURE 4. Probable dimensions of a furoxan ring associated with an aromatic system



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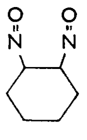
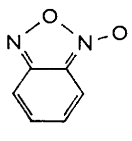
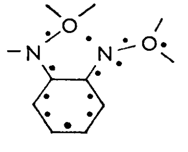
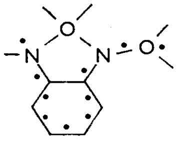
[9] D. Britton and W. E. Noland, *J. Org. Chem.*, 1962, **27**, 3218.

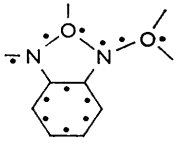
oxygen bonds in the ring are of low order, the longer being essentially single, the shorter of order 1—1·5. The nitrogen–peripheral oxygen bond is of the order 1·5—2·0. Of the earlier electronic structures suggested, (IV) is impossible and structure (V) involves carbon–nitrogen double bonds. Linnett and Rosenberg[10] have suggested (VI)—(VIII) as more probable structures. Structures (VI) and VII) are unlikely, since they involve carbon–nitrogen bonds of order higher than one and suggest a carbon–carbon bond of lower order than that found in benzene. Structure (VIII) seems to have been the most satisfactory, but it does not account for the tendency of the furoxan carbon–carbon bond to be rather shorter than those not in the furoxan system. Structure (VII) suggests a more satisfactory explanation of the rather long N′–O′ bond.


(IV)


(V)


(VI)


(VII)


(VIII)

The benzotrifuroxan molecule is not planar, each furoxan ring being twisted slightly with respect to the best plane of the benzene nucleus (Figure 3).

In the stack of polarisation-bonded molecules, the electron-acceptor molecules, benzotrifuroxan, alternate with the donor molecules, DTTD. The donor molecule has two separate donor systems, namely the two thiophen rings, which are adjacent and strictly parallel. Indeed, all the planes of all the benzotrifuroxan molecules make an angle of 9½° with the planes of the thiophen rings. The two crystallographically distinct rings, A and B, are differently related to the benzotrifuroxan. Ring A is more closely associated with a furoxan ring, and ring B with the benzene ring.

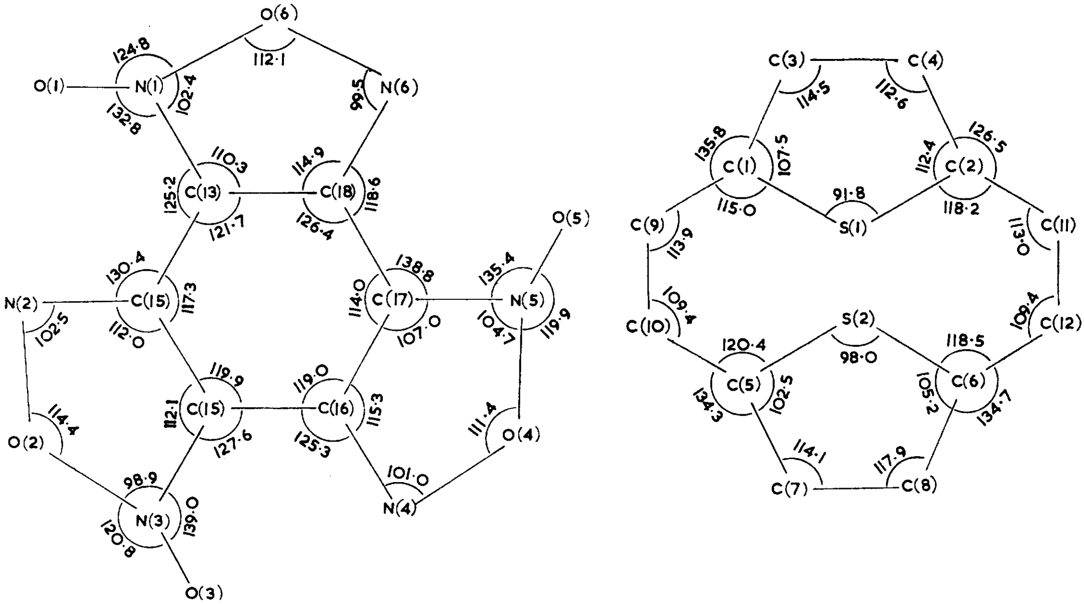


FIGURE 5. Inter-bond angles

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[10] J. W. Linnett and R. M. Rosenberg, *Tetrahedron*, 1964, **20**, 53.

EXPERIMENTAL

Preparation.—Dr. A. S. Bailey kindly supplied a sample of the adduct, prepared by the method described in 1960.[11] The 13,14-dithiatricyclo[8,2,1,$1^{4,7}$]tetradeca-4,6,10,12-tetraene was a gift from Dupont de Nemours and Co., Wilmington, Delaware.

X-*Ray Photography.*—The unit-cell dimensions were obtained from zero-layer Weissenberg photographs about *a, b*, and *c* axes, calibrated with the powder-diffraction pattern of a copper wire. The *X*-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs about the *a* axis. The intensities were corrected for Lorentz and polarisation factors, and placed on a common scale by using a limited set of values collected from zero-layer Weissenberg photographs taken about the *b* and *c* axes. No absorption or extinction corrections were applied.

Calculations.—Calculations were carried out on the Ferranti Mercury electronic computer. Structure factors and rounds of least-squares were calculated by using the SFLS programme of Rollett.[12] Atomic scattering factors for oxygen, carbon, and nitrogen were those of Berghius *et al.*; [13] for sulphur, those of Dawson,[14] and for hydrogen, those of Mc Weeny.[15] For Fourier synthesis Rollett's FATAL programme [6] and Mills's [12] general Fourier programme OSM 4 were used, and for interatomic distances and angles Spark's [12] programme.

We thank Dr. A. S. Bailey for preparing many molecular compounds of benzotrifuroxan for our use, The Wolfson Research Funds at the Royal Society and Professor D. Hodgkin for financial support to B. K., and the Oxford University Computing Laboratory (in particular Dr. J. S. Rollett) for computing facilities. Some of this work was carried out by C. K. P. whilst a guest of the Centro per Studio di Chimica Strutturistica in Rome.

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[11] A. S. Bailey, *J.*, 1960, 4710.

[12] O. S. Mills and J. S. Rollett in " Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon, London, 1961, p. 107.

[13] J. Berghius, I. M. Haanapel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendal, *Acta Cryst.*, 1955, **8**, 478.

[14] S. B. Dawson, *Acta Cryst.*, 1960, **13**, 403.

[15] R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.