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The Crystal Structure of Dibenzofuran

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The crystal and molecular structure of dibenzofuran $C_{12}H_8O$ has been determined by X-ray diffraction techniques. The space group is *Pnam* with four molecules per unit cell of dimensions $a = 7{\cdot}702 \pm 0{\cdot}010$, $b = 5{\cdot}825 \pm 0{\cdot}006$, $c = 19{\cdot}185 \pm 0{\cdot}020$ Å (at room temperature). Three-dimensional intensity data were collected with a Weissenberg type diffractometer about two crystal axes. The structure was refined by least-squares methods to a final R value of 0·073; the e.s.d.'s in bond lengths and angles not involving hydrogen atoms are about 0·003 Å and 0·13°. The anisotropic temperature factors of the C and O atoms have been accounted for by a rigid-body treatment; on this basis, corrections to the values of the observed bond distances and angles are in the ranges 0·006–0·013 Å and ±0·3°. The two benzene rings are planar with angle value of 2·2° between them. A crystallographic mirror plane normal to the c axis passes through the oxygen atom.

Introduction

This work has emerged from an E.P.R. study of the triplet state of a few organic molecules oriented in a dibenzofuran host crystal. Another purpose is to obtain precise experimental values of C–C and C–O bond lengths to be compared with theoretical models. In relation to crystal structure, we are enabled further, to explain such physical properties as cleavage, melting point and optical sign.

Experimental

The dibenzofuran crystals recrystallized from ethanol are colourless transparent plates with well developed (001) faces. The density was measured by flotation in a $ZnSO_4$ solution. The melting point is low and the crystals are sublimable. Crystal data are given in Table 1. The sample mounted for X-ray analysis (0·3 × 0·3 × 0·2 mm) was cut off a monocrystal obtained by the Bridgman–Stockbarder method. It was sealed in a Lindemann capillary. For the determination of the structure, the intensities of 700 independent reflexions belonging to layers 0–4 along **b** and 0–1 along **a**, were measured on a Weissenberg type automatic diffractometer (Stoe), with Cu $K\alpha$ radiation. After correction for Lorentz and polarization factors, the structure factors on various layers were correlated and scaled to a common base. Since $\mu R \sim 0{\cdot}2$, no absorption correction was applied. The agreement between values of structure factors of equivalent reflexions $F_e(h)$ may be used to assess the degree of internal consistency $R_c = (\sum_h \sum_e |F_e(h) - \bar{F}(h)|) / \sum_h \sum_e |F_e(h)|$. This produced an R_c value of 0·041. A Wilson plot was then made to estimate the scale factor and an overall temperature factor. The value of B was found to be 4·95 Å^2. Fig. 1 gives the distribution function of the normalized structure factors E^2 compared with theoretical curves for centro- and non-centrosymmetrical cases.

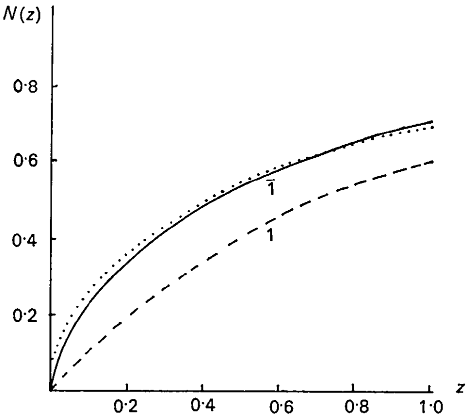

Fig. 1. Distribution function of E^2.

Table 1. *Crystal data*

Dibenzofuran
$C_{12}H_8O$
Orthorhombic
Pnam
$Z = 4$
$a = 7·702 \pm 0·010$ Å
$b = 5·825 \pm 0·006$
$c = 19·185 \pm 0·020$
$V = 860·72$ Å
$D_m = 1·29 \pm 0·01$ g.cm^{-3}
$D_x = 1·297$ g.cm^{-3}
m.p. = 86 °C
$F(000) = 352$
M.W. 168·18
$\mu = 6·40$ cm^{-1} (Cu $K\alpha$)

Table 2. *Observed and calculated structure factors* (× 10)

Unobserved intensities are indicated by an asterisk.

K	FO	FC
H=	0, L=	0
2	482	-484
4	25	35
6	32	-30
H=	0, L=	1
1	148	-194
3	107	130
5	53	53
H=	0, L=	2
0	616	-712
2	256	267
4	25	-25
6	63	58
H=	0, L=	3
1	207	261
3	237	-259
5	88	-81
H=	0, L=	4
0	432	-481
2	270	283
4	32	26
6	64	-64
H=	0, L=	5
1	151	-187
3	130	145
5	78	-87
H=	0, L=	6
0	344	-354
2	119	-125
4	32	-38
6	8*	6
H=	0, L=	7
1	225	276
3	216	-246
5	105	112
H=	0, L=	8
0	178	-188
2	306	-328
4	119	120
6	13	-3
H=	0, L=	9
1	162	-198
3	102	124
5	37	-41
H=	0, L=	10
0	155	153
2	179	177
4	174	-182
6	32	25
H=	0, L=	11
1	98	-98
3	82	84
5	77	83
H=	0, L=	12
0	96	100
2	91	-90
4	51	53
H=	0, L=	13
1	53	58
3	48	-51
5	41	-45
H=	0, L=	14
0	38	43
2	156	167
4	9*	7
H=	0, L=	15
1	154	177
3	10*	-12
5	3*	-8
H=	0, L=	16
0	8*	8
2	28	-27
4	10*	11
H=	0, L=	17
1	144	-168
3	0*	1
H=	0, L=	18
0	57	-56
2	6*	-3
4	27	25
H=	0, L=	19
1	2*	2
3	11	-8
H=	0, L=	20
0	0*	1
2	31	-35
H=	0, L=	21
1	6*	10
H=	0, L=	22
0	37	-32
H=	1, L=	0
1	722	729
2	192	182
3	181	-167
4	31	-21
5	32	36
6	33	-36
H=	1, L=	1
1	749	767
2	192	189
3	194	-175
4	15	-15
5	11*	-14
6	48	49
H=	1, L=	2
1	99	-90
2	37	40
3	6*	7
4	94	86
5	21	12
6	76	78
H=	1, L=	3
1	225	235
2	52	50
3	93	-94
4	130	-124
5	101	99
6	26	-29
H=	1, L=	4
1	36	-31
2	102	-110
3	156	142
4	9*	16
5	69	-60
6	53	-56
H=	1, L=	5
1	175	165
2	16	10
3	216	215
4	49	49
5	85	-79
6	34	-33
H=	1, L=	6
1	176	-177
2	120	118
3	27	-25
4	70	-73
5	33	31
6	28	-26
H=	1, L=	7
1	61	59
2	85	-84
3	18	-22
4	4*	3
5	21	-19
6	29	30
H=	1, L=	8
1	150	-147
2	99	-98
3	9*	-10
4	37	-34
5	10*	11
6	32	28
H=	1, L=	9
1	315	-309
2	47	-50
3	36	39
4	0*	-7
5	44	45
6	8*	5
H=	1, L=	10
1	136	124
2	41	48
3	37	-34
4	57	-57
5	32	-37
6	15	-13
H=	1, L=	11
1	70	60
2	14	13
3	102	-102
4	75	77
5	0*	-9
H=	1, L=	12
1	0*	1
2	49	-50
3	46	-50
4	128	125
5	31	35
H=	1, L=	13
1	61	-64
2	17	16
3	27	-27
4	59	-62
5	10*	-7
H=	1, L=	14
1	77	76
2	16	-19
3	38	39
4	13*	-11
5	7*	-14
H=	1, L=	15
1	73	67
2	69	70
3	38	40
4	11*	-8
5	5*	-7
H=	1, L=	16
1	41	-39
2	96	101
3	32	34
4	15	-17
H=	1, L=	17
1	46	46
2	48	-52
3	0*	-3
4	0*	6
H=	1, L=	18
1	15	-12
2	32	-37
3	12*	7
4	18	-15
H=	1, L=	19
1	0*	2
2	20	-17
3	21	22
4	8	7
H=	1, L=	20
1	1*	-1
2	16	-20
3	20	-20
H=	1, L=	21
1	2*	-5
2	8*	4
H=	1, L=	22
1	11*	-10
H=	2, L=	0
0	703	-760
1	446	-420
2	65	77
3	49	56
4	7	-1
H=	2, L=	1
0	930	1074
1	823	942
2	70	27
3	122	-142
4	35	-38
H=	2, L=	2
0	235	265
1	100	90
2	195	-225
3	74	79
4	11	0
H=	2, L=	3
0	331	319
1	114	109
2	106	-95
3	75	71
4	23	28
H=	2, L=	4
0	76	-94
1	151	155
2	82	95
3	91	-98
4	39	-46
H=	2, L=	5
0	114	87
1	110	-104
2	278	276
3	29	34
4	30	-34
H=	2, L=	6
0	284	296
1	44	38
2	95	-106
3	57	61
4	112	124
H=	2, L=	7
0	78	80
1	119	-114
2	26	-34
3	112	112
4	18	24
H=	2, L=	8
0	125	-153
1	11	-16
2	251	267
3	29	-32
4	54	-108
H=	2, L=	9
0	375	-364
1	77	74
2	113	-91
3	195	-193
4	66	61
H=	2, L=	10
0	70	-51
1	12	4
2	27	-32
3	89	-84
4	63	66
H=	2, L=	11
0	62	12
1	49	-44
2	39	34
3	72	63
4	57	-57
H=	2, L=	12
0	88	85
1	87	-85
2	73	-70
3	98	99
4	25	-29
H=	2, L=	13
0	11	-14
1	68	62
2	105	-102
3	29	-23
4	14	-14
H=	2, L=	14
0	15	17
1	0*	-6
2	64	-65
3	40	-39
4	6*	-4
H=	2, L=	15
0	123	128
1	63	-64
2	46	37
3	31	34
4	3*	2
H=	2, L=	16
0	144	-157
1	97	101
2	74	77
3	29	27
4	10	-8
H=	2, L=	17
0	0*	-14
1	47	48
2	39	41
3	17	16
4	15	-13
H=	2, L=	18
0	69	77
1	22	-27
2	24	-26
3	7	-9
4	8	8
H=	2, L=	19
0	7*	-9
1	15	-17
2	15	17
3	5*	-4
H=	2, L=	20
0	19	22
1	18	-22
2	7	5
3	0*	-2
H=	2, L=	21
0	9	6
1	9	7
2	6*	-5
H=	2, L=	22
0	14	13
H=	3, L=	0
1	586	-585
2	540	-543
3	31	20
4	86	82
H=	3, L=	1
1	106	107
2	72	69
3	13	5
4	61	-72
H=	3, L=	2
1	77	71
2	106	96
3	48	-50
4	42	46
H=	3, L=	3
1	45	-48
2	101	93
3	71	-63
4	69	90
H=	3, L=	4
1	20	-19
2	175	175
3	43	-36
4	167	-175
H=	3, L=	5
1	73	74
2	38	-31
3	36	-43
4	42	44
H=	3, L=	6
1	140	133
2	13	14
3	60	60
4	59	63
H=	3, L=	7
1	59	-54
2	60	60
3	41	44
4	14	-16
H=	3, L=	8
1	202	196
2	88	90
3	11	11
4	38	36
H=	3, L=	9
1	34	-30
2	47	-47
3	7*	4
4	6*	-9
H=	3, L=	10
1	131	-117
2	155	-151
3	61	60
4	6*	-7
H=	3, L=	11
1	1*	-5
2	10	-14
3	97	101
4	59	-57
H=	3, L=	12
1	14	13
2	22	18
3	24	-27
4	13	19
H=	3, L=	13
1	0*	0
2	12	16
3	83	-84
4	27	26
H=	3, L=	14
1	86	-83
2	21	-19
3	58	-55
4	30	-36
H=	3, L=	15
1	64	65
2	35	-35
3	48	-50
4	4*	3
H=	3, L=	16
1	7*	-8
2	28	27
3	16	16
4	4*	2
H=	3, L=	17
1	47	-52
2	48	51
3	31	38
4	22	23
H=	3, L=	18
1	23	22
2	23	20
3	13	-13
H=	3, L=	19
1	5*	-7
2	5*	-4
3	20	19
H=	3, L=	20
1	17	18
2	7	-8
H=	3, L=	21
1	6*	8
H=	4, L=	0
0	25	31
2	291	-301
3	35	-41
4	45	43
H=	4, L=	1
0	7	-21
1	419	-420
2	176	-167
3	17	-9
4	79	84
H=	4, L=	2
0	89	-84
1	70	53
2	172	164
3	17	-16
4	26	-22
H=	4, L=	3
0	2*	1
1	10	6
2	98	-104
3	39	33
4	65	-63
H=	4, L=	4
0	42	-38
1	189	196
2	81	-76
3	61	-65
4	25	20
H=	4, L=	5
0	146	-146
1	16	-14
2	30	-20
3	27	-26
4	44	-49
H=	4, L=	6
0	72	61
1	76	-88
2	92	95
3	86	95
4	64	-63
H=	4, L=	7
0	44	-48
1	148	167
2	24	-26
3	67	-75
4	58	65
H=	4, L=	8
0	205	195
1	104	115
2	69	-68
3	67	58
4	62	63
H=	4, L=	9
0	148	143
1	10	-21
2	31	32
3	124	130
4	4*	-6
H=	4, L=	10
0	135	-134
1	40	-47
2	28	27
3	63	-60
4	26	-23
H=	4, L=	11
0	94	-82
1	42	-42
2	114	109
3	80	-81
4	0*	5
H=	4, L=	12
0	6*	-2
1	54	-52
2	47	51
3	5*	1
4	19	16
H=	4, L=	13
0	90	89
1	18	-17
2	33	-33
3	45	49
4	18	15
H=	4, L=	14
0	109	-107
1	13	7
2	28	-27
3	17	-17
4	3*	-4
H=	4, L=	15
0	27	30
1	15	16
2	47	-46
3	53	-53
4	18	-19
H=	4, L=	16
0	113	121
1	19	20
2	37	-39
3	30	-29
4	0*	-5
H=	4, L=	17
0	91	-59
1	19	-21
2	12	11
3	25	26
H=	4, L=	18
0	27	-29
1	5*	8
2	8	7
3	37	39
H=	4, L=	19
0	12	-13
1	21	20
2	9	-7
H=	4, L=	20
0	4*	-5
1	4*	-7
H=	5, L=	0
1	17	20
2	56	51
3	15	5
4	35	38
H=	5, L=	1
1	70	-72
2	261	-263
3	103	-106
4	4*	6
H=	5, L=	2
1	49	50
2	59	-52
3	70	75
4	64	-73
H=	5, L=	3
1	34	34
2	59	-56
3	67	-71
4	49	46
H=	5, L=	4
1	24	-22
2	8	2
3	43	-43
4	46	55
H=	5, L=	5
1	127	-122
2	4*	-1
3	46	46
4	67	-68
H=	5, L=	6
1	12	12
2	0*	4
3	63	-64
4	14	12
H=	5, L=	7
1	0*	-2
2	18	-18
3	10	-7
4	9	-11
H=	5, L=	8
1	53	-47
2	12	12
3	9	9
4	18	-18
H=	5, L=	9
1	66	62
2	149	148
3	19	18
4	15	23
H=	5, L=	10
1	12	-8
2	56	59
3	30	-29
4	0*	-2
H=	5, L=	11
1	3*	6
2	55	-53
3	9	-5
4	0*	-1
H=	5, L=	12
1	17	15
2	73	-76
3	69	72
4	15	14
H=	5, L=	13
1	47	45
2	11	-8
3	28	23
4	36	38
H=	5, L=	14
1	8*	-9
2	9	13
3	9	11
4	8	9
H=	5, L=	15
1	40	-40
2	24	-23
3	14	-10
H=	5, L=	16
1	57	57
2	0*	6
3	33	-33
H=	5, L=	17
1	6*	-3
2	15	-14
H=	5, L=	18
1	22	-24
H=	6, L=	0
0	193	-185
1	117	121
2	212	228
3	150	160
4	29	-27
H=	6, L=	1
0	43	32
1	24	-3
2	88	-87
3	34	-34
4	20	-24
H=	6, L=	2
0	89	91
1	30	-36
2	38	-39
3	88	-86
4	46	50
H=	6, L=	3
0	72	82
1	84	-77
2	30	28
3	6*	-8
4	32	35
H=	6, L=	4
0	55	39
1	16	-12
2	55	-59
3	41	39
4	9*	-8
H=	6, L=	5
0	104	-109
1	37	39
2	40	42
3	60	-62
4	6*	-11
H=	6, L=	6
0	21	-15
1	26	-26
2	36	-39
3	10	-10
4	28	-35
H=	6, L=	7
0	69	81
1	72	-72
2	29	-37
3	52	52
4	22	-20
H=	6, L=	8
0	107	-119
1	48	-46
2	19	23
3	54	-62
4	29	-27
H=	6, L=	9
0	0*	-9
1	90	89
2	0*	7
3	0*	-1
4	23	20
H=	6, L=	10
0	25	23
1	112	104
2	40	-39
3	34	42
4	37	33
H=	6, L=	11
0	28	-29
1	32	30
2	31	-32
3	4*	2
4	15	-15
H=	6, L=	12
0	28	-24
1	55	-50
2	41	42
3	6*	-7
4	8	-6
H=	6, L=	13
0	33	33
1	34	-36
2	32	34
3	10	11
H=	6, L=	14
0	52	52
1	13	10
2	9	7
3	27	29
H=	6, L=	15
0	47	-47
1	48	-49
2	10	-9
H=	6, L=	16
0	19	20
1	11	13
H=	7, L=	0
1	27	-25
2	91	98
3	109	124
4	47	52
H=	7, L=	1
1	28	-28
2	65	71
3	13	13
4	38	40
H=	7, L=	2
1	16	-13
2	26	-26
3	33	-38
4	13	-10
H=	7, L=	3
1	31	30
2	40	-44
3	71	79
4	14	-18
H=	7, L=	4
1	53	54
2	22	24
3	34	-35
4	9	-11
H=	7, L=	5
1	18	19
2	9	11
3	4*	-3
4	5*	7
H=	7, L=	6
1	29	-29
2	43	-44
3	17	17
4	2*	0
H=	7, L=	7
1	22	22
2	22	19
3	32	-36
4	7	9
H=	7, L=	8
1	0*	8
2	50	-55
3	28	-27
4	9	-11
H=	7, L=	9
1	8*	-5
2	43	-46
3	12	-11
H=	7, L=	10
1	13	-10
2	42	47
3	29	27
H=	7, L=	11
1	50	-50
2	54	58
3	0*	-2
H=	7, L=	12
1	27	-25
2	14	14
H=	7, L=	13
1	9*	10
2	25	-30
H=	7, L=	14
1	31	33
H=	8, L=	0
0	10	11
1	6*	-1
2	15	17
3	18	-15
H=	8, L=	1
0	62	-70
1	29	-22
2	29	36
3	95	106
H=	8, L=	2
0	44	-49
1	18	17
2	32	-37
3	23	26
H=	8, L=	3
0	29	-31
1	18	-20
2	36	36
3	20	-19
H=	8, L=	4
0	45	49
1	0*	-3
2	7	6
3	10	-14
H=	8, L=	5
0	44	52
1	43	45
2	14	-14
3	5*	5
H=	8, L=	6
0	42	-47
1	26	-28
2	43	47
H=	8, L=	7
0	0*	-2
1	17	20
2	3*	-2
H=	8, L=	8
0	55	62
1	0*	7
2	27	-29
H=	8, L=	9
0	38	38
1	65	-68
H=	8, L=	10
0	18	18
1	13	-13
H=	9, L=	0
1	29	34

Table 3. *The heavy atom parameters and their standard deviations*

All the values in the table have been multiplied by 10^4. The temperature factor is in the form
$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	2427 (3)	2351 (4)	2500*	234 (4)	319 (7)	46 (1)	−109 (9)	0*	0*
C(1)	2939 (2)	3653 (4)	1927 (1)	153 (3)	322 (7)	41 (2)	40 (7)	4 (2)	23 (4)
C(2)	2647 (3)	3045 (5)	1244 (1)	196 (4)	347 (9)	52 (1)	3 (9)	−31 (3)	−66 (4)
C(3)	3222 (3)	4550 (5)	741 (1)	214 (4)	600 (12)	35 (1)	173 (11)	−32 (3)	−51 (4)
C(4)	4034 (3)	6559 (5)	923 (1)	207 (4)	517 (10)	39 (1)	108 (11)	10 (3)	64 (4)
C(5)	4306 (3)	7161 (4)	1609 (1)	165 (3)	359 (7)	45 (1)	12 (8)	−2 (2)	16 (3)
C(6)	3741 (2)	5678 (3)	2117 (1)	125 (2)	311 (7)	38 (1)	57 (8)	− 13 (2)	−19 (3)

* Parameter constrained by symmetry requirements.

Determination and refinement of the structure

The position of the molecule in the unit cell was found by analogy with carbazole $C_{12}H_8NH$ of which the crystal structure has been determined by Kurahashi, Fukuyo & Shimada (1969), crystal data and formal configuration of carbazole and dibenzofuran being close.

A set of structure factors calculated on this basis produced an $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ value of 0·25. The positional and isotropic parameters of all non-hydrogen atoms were refined by least-squares with a block diagonal approximation to the normal equation (4×4 blocks for x, y, z and B of each atom) using a unitary weighting scheme and with scattering factors obtained from Hanson, Herman, Lea & Skillman (1964). After two cycles of refinement ($R=0{\cdot}17$) isotropic parameters of hydrogen atoms and anisotropic thermal parameters of the other atoms were introduced; the weighting scheme was changed to

$$W^{-1}=1+[(|F_o|-2{\cdot}5)/1{\cdot}5]^2$$

so that $\langle W\Delta^2\rangle$ was constant over the whole range of $|F_o|$ values. After some cycles of refinement, R was reduced to 0·073. All the calculations were carried out on an IBM 360/65 computer, using the N.R.C. crystallographic programs written by Ahmed, Hall, Pippy & Saunderson (1969).

Results and corrections for thermal motion

The observed and calculated structure factors are listed in Table 2; the final parameters of O and C atoms are given in Table 3 and of hydrogen atoms in Table 4. The standard deviations in the coordinates of the heavier atoms and of the hydrogen atoms are of the order of 0·0025 and 0·03 Å respectively; the corresponding standard deviations in C–C and C–O distances are around 0.003 Å and in angles 0·2°. Shomaker & Trueblood's (1968) treatment of the rigid-body motion of molecules in crystals in terms of tensors **T**, **L** and **S** has been applied to dibenzofuran. These tensors were refined from a least-squares treatment with equal weights assigned to all thermal factors. The results are given in Table 5. The agreement between observed and calculated U_{ij} for each atom is good, the difference scarcely exceeding the standard deviation. Corrections to intramolecular C–C and C–O distances and angles for thermal motion have been derived from the tensor **L** according to Johnson (1969) using a modified version of *ORFFE* (Busing, Martin & Levy, 1962). Uncorrected and corrected values for all bond distances and angles are given in Table 6.

Table 4. *Parameters for the hydrogen atoms and their standard deviations* (×10^3)

	x	y	z	B
H(1)	0·208 (3)	0·162 (5)	0·114 (1)	4·8 (5)
H(2)	0·314 (3)	0·418 (5)	0·025 (2)	4·9 (6)
H(3)	0·460 (3)	0·748 (4)	0·054 (2)	3·9 (6)
H(4)	0·488 (4)	0·854 (5)	0·171 (1)	3·2 (5)

Table 5. *Rigid-body tensors for dibenzofuran referred to a Cartesian coordinate system, whose origin coincides with the oxygen position and directions with the crystallographic axis*

Standard deviations are given in brackets.

T (Å^2)	672 (73)	−146 (55)	0	(unreduced)
(×10^4)		490 (52)	0	
			1006 (44)	
L (rad^2)	52 (6)	−32 (6)	0	
(×10^4)		25 (7)	0	
			120 (38)	
S (Å. rad)	0	0	−116 (15)	
(×10^4)	0	0	104 (16)	
	206 (59)	−98 (36)	0	

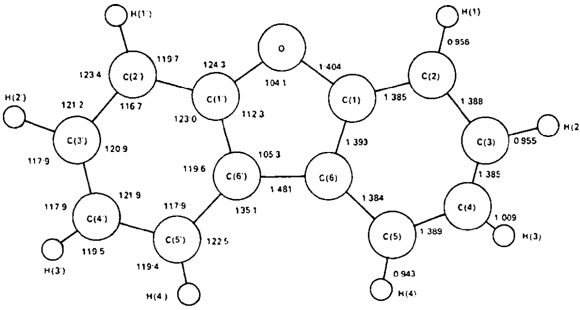

Fig. 2. Bond lengths and angles of dibenzofuran (values are corrected for thermal motion).

Table 6. *Bond distances and angles in the molecule*

The two values relate to uncorrected and corrected values respectively for thermal motion. No correction has been applied to data involving hydrogen atoms.

C(1)–C(2)	1·379 (3) Å	1·385 Å	C(2)–H(1)	0·956 (26) Å
C(2)–C(3)	1·379 (4)	1·388	C(3)–H(2)	0·955 (26)
C(3)–C(4)	1·372 (4)	1·385	C(4)–H(3)	1·009 (27)
C(4)–C(5)	1·383 (3)	1·389	C(5)–H(4)	0·943 (27)
C(5)–C(6)	1·375 (3)	1·384		
C(6)–C(1)	1·381 (3)	1·393		
C(6)–C(6′)	1·475 (3)	1·481		
C(1)–O	1·396 (3)	1·404		
C(1)–O——C(1′)	104·5 (0·2)°	104·1°		
O——C(1)–C(2)	124·6 (0·2)	124·3		
O——C(1)–C(6)	112·4 (0·2)	112·7		
C(6)–C(1)–C(2)	123·0 (0·2)	123·0		
C(1)–C(2)–C(3)	117·0 (0·2)	116·7		
C(2)–C(3)–C(4)	120·7 (0·2)	120·9		
C(3)–C(4)–C(5)	121·9 (0·2)	121·9		
C(4)–C(5)–C(6)	118·0 (0·2)	117·9		
C(5)–C(6)–C(1)	119·4 (0·2)	119·6		
C(5)–C(6)–C(6′)	135·3 (0·2)	135·1		
C(1)–C(6)–C(6′)	105·4 (0·2)	105·3		
C(1)–C(2)–H(1)	119·7°		C(3)–C(4)–H(3)	117·9°
C(3)–C(2)–H(1)	123·4		C(5)–C(4)–H(3)	119·5
C(2)–C(3)–H(2)	121·3		C(4)–C(5)–H(4)	119·4
C(4)–C(3)–H(2)	117·9		C(6)–C(5)–H(4)	122·5

Distances are increased by quantities (in the range 0·006–0·013 Å) which are significantly greater than standard deviations; corrections of the angle (0·0–0·3°) are negligible. Bond angles and distances are given with the atom designations in Fig. 2. The configuration of the molecule, including the 50% probability thermal vibration ellipsoids of the non-hydrogen atoms drawn with *ORTEP* (Johnson, 1965), is shown in Fig. 3.

Table 7. *Equations of the planes, χ^2 results and angles between different planes*

1.	Benzene ring plane (1)	$\chi^2 = 13·99$
2.	Benzene ring plane (2)	$\chi^2 = 13·99$
3.	Furan ring plane	$\chi^2 = 0·48$

Equations of planes

1. $0·8843x - 0·4665y - 0·0194z - 0·9398 = 0$
2. $-0·8843x + 0·4665y - 0·0194z + 1·1267 = 0$
3. $0·8854x - 0·4648y \quad - 1·0240 = 0$

Angles between different planes

	2	3
1.	2·23	1·12
2.		1·12

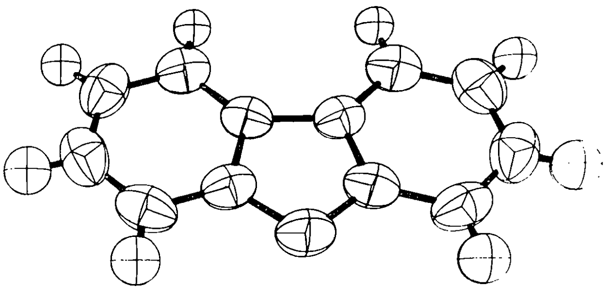

Fig. 3. The configuration of dibenzofuran molecule including the 50% probability thermal vibration ellipsoids of the non-hydrogen atoms.

Table 8. *Deviations of atoms from various planes and standard deviations in parentheses* (× 10³)

The least squares plane is determined by the atoms marked by an asterisk.

	1	2	3
O	−0·013 (2) Å	0·013 (2) Å	0·001 (2)Å*
C(1)	0·005 (2)*	0·037 (2)	−0·001 (2)*
C(2)	−0·004 (2)*	0·097 (2)	−0·036 (2)
C(3)	−0·000 (2)*	0·132 (2)	−0·050 (2)
C(4)	0·002 (2)*	0·115 (2)	−0·037 (2)
C(5)	−0·001 (2)*	0·067 (2)	−0·014 (2)
C(6)	−0·003 (2)*	0·032 (2)	0·000 (2)*
C(6′)	−0·032 (2)	0·003 (2)*	0·000 (2)*
C(5′)	−0·067 (2)	0·001 (2)*	−0·014 (2)
C(4′)	−0·115 (2)	−0·002 (2)*	−0·037 (2)
C(3′)	−0·132 (2)	0·000 (2)*	−0·050 (2)
C(2′)	−0·097 (2)	0·004 (2)*	−0·036 (2)
C(1′)	−0·037 (2)	−0·005 (2)*	−0·001 (2)*
H(1)	−0·001 (23)	0·103 (23)	−0·039 (23)
H(2)	0·066 (26)	0·102 (26)	−0·002 (26)
H(3)	0·154 (22)	−0·008 (22)	0·101 (22)
H(4)	0·013 (28)	0·046 (28)	0·005 (28)
H(4′)	−0·046 (28)	−0·013 (28)	0·005 (28)
H(3′)	0·008 (22)	−0·154 (22)	0·101 (22)
H(2′)	−0·102 (26)	−0·066 (26)	−0·002 (26)
H(1′)	−0·103 (23)	0·001 (23)	−0·039 (23)

Discussion

The individual five- and six-membered rings are strictly planar, but the molecule as a whole shows a small, but significant, deviation from planarity. The dihedral angles between the five-membered ring and the six-membered rings are 1·12°. These small deviations from exact planarity are very similar to those observed in carbazole (1·0°), dibenzothiophene (0·4 and 1·2°) and dibenzoselenophene (0·5, 1·1, 1·2 and 1·2°). The mean values for the bond distances and valency angles in dibenzofuran are compared with those in carbazole, dibenzothiophene, dibenzoselenophene and biphenyl in Table 9. The distances and angles are very similar in those molecules, except of course C–X lengths and C–X–C angles; the angles in the five-membered rings show larger differences. The observed C–O bond distance (1·404 Å), is significantly shorter than in the paraffinic and saturated heterocycles (1·426 Å: Sutton, 1965). C–X lengths and C–X–C angles in furan and dibenzofuran groups are compared in Table 10. The benzene rings decrease the conjugation effect. The packing of the molecules in the unit cell is shown in Fig. 4. It seems to be uniform in **a** and **b** directions, and close contacts of 3·72–3·76 Å between molecules are found for any pair of neighbouring molecules; but there is a large space around $z=0$ and $z=c/2$. This is the reason why the compound grows in very thin crystals showing excellent cleavage parallel to the (001) plane. Fluorene, carbazole and dibenzofuran crystals belong to the same space group and the angles between the mean plane of the molecules and the a axis are respectively 55·2, 61·0 and 62·3°. The positive optical sign of dibenzofuran is explained by the crossed packing of the molecules, as shown in Fig. 4.

Table 9. *A comparison of bond distances and angles in compounds smilar to dibenzofuran*

	C–O	C–HN*	C–S†	C–Se‡	Biphenyl§
C(1)–C(2)	1·385 Å	1·395 Å	1·384 Å	1·395 Å	1·398
C(2)–C(3)	1·388	1·390	1·384	1·371	1·387
C(3)–C(4)	1·385	1·398	1·385	1·377	1·379
C(4)–C(5)	1·389	1·395	1·370	1·380	1·379
C(5)–C(6)	1·384	1·400	1·392	1·395	1·387
C(6)–C(6′)	1·481	1·467	1·441	1·453	1·497
C(1)–C(6)	1·393	1·404	1·409	1·398	1·398
C(1)–X	1·404	1·414	1·740	1·899	
C(1)–X——C(1′)	104·1°	108·3°	91·5°	86·6°	
X——C(1)–C(6)	112·3	108·8	112·3	112·4	
C(1)–C(2)–C(3)	116·7	117·7	117·8	118·7	
C(2)–C(3)–C(4)	120·9	121·3	121·6	121·1	
C(3)–C(4)–C(5)	121·9	120·4	120·5	120·6	
C(4)–C(5)–C(6)	117·9	119·5	120·0	120·3	
C(5)–C(6)–C(1)	119·6	118·8	118·7	118·1	
C(6)–C(1)–C(2)	123·0	122·3	121·6	121·6	
C(1)–C(6)–C(6′)	105·3	107·1	111·9	114·3	

* Kurahashi, Fukuyo & Shimada (1969).
† Schaffrin & Trotter (1970).
‡ Hope, Knobler & McCullough (1970).
§ Robertson (1961).

Table 10. *A comparison of* C–X *bond lengths and* C–X–C *angles for the furan group and the dibenzofuran group*

	C–X	C–X–C
Furan*	1·362 Å	106·55°
Thiophene*	1·714	92·17
Selenophene*	1·8763	87·72
Dibenzofuran	1·404 Å	104·1°
Dibenzothiophene†	1·740	91·5
Dibenzoselenophene‡	1·899	86·7

* Brown, Burden & Godfrey (1968).
‡ Hope, Knobler & McCullough (1970).
† Schaffrin & Trotter (1970).

Table 11. *Intermolecular distances less than* 3·8 Å

Contacts with hydrogen atoms are excluded.

Atom 1	Atom 2	Tr	$s(i)$	Distance
C(1)	O	000	2	3·687 Å
C(1)	C(5)	$\bar{1}00$	2	3·768
C(5)	C(1)	010	2	3·768
C(5)	C(2)	010	1	3·724
C(5)	C(6)	$\bar{1}\bar{1}0$	2	3·780
C(5)	O	010	1	3·765
C(6)	O	000	2	3·431

* 'Tr' refers to unit translations along the crystallographic axis. $s(i)$ refers to the symmetry elements of the space group

$s(1)=x\ y\ z$
$s(2)=\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}-z$

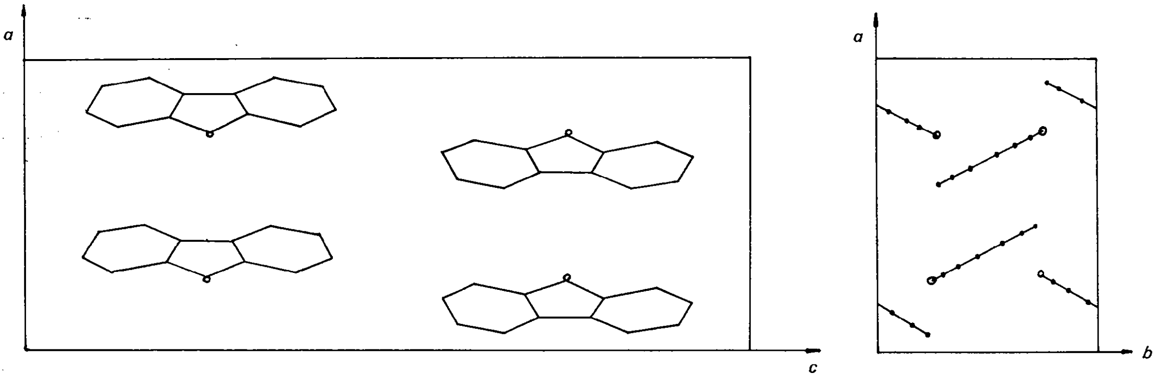

Fig. 4. Projections of the structure along b and c axes.

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The Crystal Structures of Allitol and D-Iditol

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The crystal structures of two hexitols, allitol and D-iditol, $C_6H_{14}O_6$, have been determined with Cu $K\alpha$ radiation, using direct methods and the tangent formula for phase determination. The crystal data are: for allitol, $P2_1/c$ with $a=4{\cdot}708$ (3), $b=13{\cdot}408$ (8), $c=6{\cdot}616$ (4) Å; $\beta=100{\cdot}1°$; $Z=2$; $D_m=1{\cdot}482$, $D_x=1{\cdot}472$ g.cm^{-3}; for D-iditol, $P2_1$ with $a=8{\cdot}124$ (2), $b=8{\cdot}386$ (3), $c=5{\cdot}870$ (3) Å; $\beta=93{\cdot}82°$, $Z=2$; $D_m=1{\cdot}516$, $D_x=1{\cdot}510$ g.cm^{-3}. Both molecules have bent chain conformations as predicted from previous studies of alditol structures. That of allitol has a crystallographic center of symmetry. The bond lengths and angles are normal, with mean values over both structures of C–C = 1·523, C–O = 1·422 Å, C–C–C = 113·3, C–C–O = 109·8°. All hydrogen bonding is intermolecular. That of allitol is normal with each hydroxyl acting as donor and acceptor to form infinite chains. That of D-iditol is unusual for the alditol series in that the hydrogen bonding consists of infinite chains with branched chains. This requires that one hydroxyl is a donor only and that another is a double acceptor as well as a donor.

Introduction

These two structure determinations are part of a study of the pentitols and hexitols which has included D,L-arabinitol (Hunter & Rosenstein, 1968), ribitol (Kim, Jeffrey & Rosenstein, 1969), xylitol (Kim & Jeffrey, 1969), D-mannitol (Berman, Jeffrey & Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1968) galactitol (Berman & Rosenstein, 1968), and D-glucitol (Park, Jeffrey & Hamilton, 1971).

All the stereoisomers, three pentitols and six hexitols, have now been examined except D-altritol. Several are reported to exist in different polymorphic modifications, of which only those of D-mannitol have been studied in detail. Allitol occurs naturally in certain plants. D-iditol is a synthetic product. The naturally occurring form is the L stereoisomer which is found with D-glucitol in mountain ash berries. No polymorphs have been reported for either of these hexitols.

From previous work it has been predicted by Jeffrey & Kim (1970) that in the crystalline state neither allitol nor D-iditol will have the straight-chain conformations shown in I(*A*) and II(*A*), respectively. In allitol, the unique bent chain centrosymmetrical conformation I(*B*) was predicted, while in D-iditol, it was postulated that the conformation II(*B*) would be preferred over II(*C*).

The primary purpose of these structure determinations was to verify these predictions and to study the intermolecular hydrogen bonding and molecular packing.